

Scientific & Industrial Glass
Blowing & Lab. Techniques

BARR

CFTRI-MYSORE



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1. multiple glass seals
2. glass apparatus
3. metal seals ⑨ distillation equipments
4. high vacuum
5. vacuum gages
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7. gas ~~ad~~sorption apparatus
8. swietoslowski ebulliometers
9. glassblowing

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Scientific and Industrial Glass Blowing and Laboratory Techniques

by

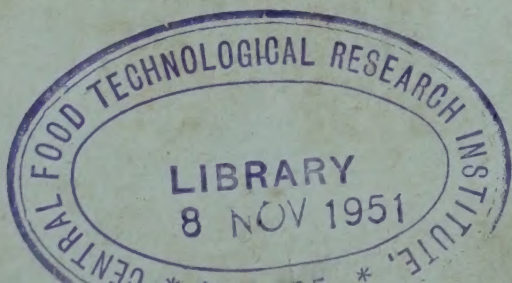
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and

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Gulf Research and Development Company

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Scientific and I.

FOREWORD

IN this age of science, nearly everything we use and do has been improved by research. We are well aware of our debt to the men who have so raised our standard of living, but few of us realize that their research is absolutely dependent on the men who work glass.

Without glass, the development of our technologic culture would certainly have taken a very different course. Its unique, well-known chemical and physical properties make it a necessity in nearly all lines of experimentation.

The history of scientific glassware has passed through three rather definite stages. From the beginning of science to the end of the last century, only the simplest glass apparatus was known; flasks and retorts and tubes were used, and they changed very little in form through the ages. Then more complicated unit apparatus was introduced, such as all-glass condensers, multiple-necked flasks, and elaborate automatic extraction devices. These were standardized and manufactured for specialized uses, and they were rarely altered. Finally, the last quarter century has been marked by the development of custom-made glassware. Through close coöperation between the workers in glass and in research, large and complicated apparatus, especially designed for the problem at hand, can be built quickly and easily. Rubber hose connections have given way to all-glass construction, to great advantage, and now it is usual to see a laboratory almost filled with one vine-like piece of glass.

The purpose of this book is to aid the experimentalist in using glass; it should do so in two ways. First it should teach him, with moderate practice, to perform the simple operations himself. Skill in making small seals is now required in many types of laboratory work, because such construction is required very frequently in connection with assembly, alteration, and repair of apparatus, and a professional glass blower is rarely available on short notice. In so doing, the experimentalist in no way competes with the expert glass worker, but relieves him for difficult work. Very few scientific workers become highly skilled in working glass, and it is not necessary that they do, but some knowledge of the art is becoming more and more important.

This book will also help the laboratory worker design complex equipment more intelligently. The services of an expert glass blower are of little use unless they are understood by the man who designs and uses the equipment. The

more advanced portions of this book are intended to explain what the professional can do, rather than the details of how he does it, which can only be learned by long practice.

In brief, this book tells about the glass blower's fire which are older than Aladdin's Lamp, and have already wrought greater miracles.

JOHN R. BOWMAN

Mellon Institute of Industrial Research

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THIS BOOK IS DEDICATED TO THE MEMORY OF CHRISTOPHER KIRWER, WHO IN 1943, RECEIVED THE WESTINGHOUSE ORDER OF MERIT AND THE SILVER "W" FOR HIS ABILITY TO PRODUCE GLASS APPARATUS REQUIRING AN UNUSUAL DEGREE OF SKILL AND INGENUITY; FOR HIS TALENT IN INTERPRETING THE SPECIAL NEEDS OF A RESEARCH LABORATORY IN THIS FIELD; AND FOR HIS SUCCESS IN TRAINING YOUNG MEN IN DIFFICULT GLASSBLOWING TASKS.

AUTHORS' PREFACE

It is generally recognized that the most important construction materials for scientific equipment are the laboratory glasses now available. The utility and versatility of glass far exceeds that of other materials used at the present time. Visibility, chemical inertness and ease in shaping and forming equipment are a few of the many advantages responsible for the universal adoption of glass. The extensive use of glass has required personnel skilled in the art of making and repairing glass equipment. The training of such persons is varied. Many have served long apprenticeships under competent glass blowers and are capable of making complex glass equipment. In the majority, however, are the persons who have had short courses in educational institutions or by necessity have had resort to self instruction to make and repair equipment used in their scientific researches. We feel that a comprehensive description of glass blowing along with suggestions of glass shop facilities will be very helpful to all personnel engaged in making glass equipment, especially the beginner apprentice.

In presenting this book we are attempting to fulfill three objectives. First, it is necessary to point out and describe characteristics of various laboratory glasses as well as the fundamental techniques involved in handling glass. We have purposely outlined these techniques in detail so that a beginner has every opportunity to become accustomed to the simplest procedures of handling glass. Once the student masters these techniques he will find that the production of complicated equipment is not difficult. We have included glass-to-metal seals as one of the more advanced of these fundamental techniques because they are required in the production of laboratory equipment.

Our second objective is to present advanced techniques in the application of high vacuum, silvering and the evacuation of glass jackets to the construction of glass equipment. It is our opinion that no course for training personnel is complete unless these techniques are mastered and thoroughly understood. We have presented high vacuum in detail because of its application in other fields of scientific research. Several condensation pumps which are used with mechanical vacuum pumps are described along with auxiliary equipment needed in vacuum work.

Our third objective is to describe glass equipment for specific applications in the laboratory. These examples are

but a few of the many types used in scientific research. We claim no originality for many of the examples cited because they have been described in the scientific literature. These examples are described in detail to show the importance of glass equipment in scientific research, to present design and operating techniques and finally to challenge the imagination of the student to design better and more flexible equipment.

In preparing the manuscripts for this book, we have obtained information and illustrations from members of the staff at Corning Glass Works; Distillation Products, Inc.; Westinghouse Electric Corp.; Podbielniak, Inc.; Fisher Scientific Company; Precision Scientific Company; Litton Engineering Laboratories; Eisler Engineering Company; American Instrument Company; W. M. Welch Scientific Company and Radio Corporation of America. We are grateful to all of these organizations for their assistance.

There are many individuals to whom we are obligated. Dr. John R. Bowman, Dr. W. E. Hanson, Dr. B. W. Warner, Dr. J. R. Anderson, Dr. L. G. Joyner, Dr. C. W. Montgomery, Dr. R. Davis, Mr. E. H. Epprecht and Mr. R. O. Clark have all contributed sections pertaining to specific laboratory equipment. We are indebted to Mr. John T. Madison for the illustrations of Chapter I, to Mr. W. S. Lockard for the ebulliometer drawings, to Mr. C. G. Denninger for drawings of distillation equipment, to Mr. Richard P. Jones for general drawing supervision as well as the remainder of the drawings, and to Mr. Clifford E. Boden for photographs included in the book. Mr. William Kravenko was responsible for the typing of the manuscript.

Lastly, we are deeply grateful to Dr. Paul D. Foote and Mr. Eugene Ayres for their interest in making this book possible, to Dr. Gordon H. Stillson for reading the manuscript and to the members on the staff of Gulf Research and Development Company who have unselfishly contributed information for this book.

CHAPTER I.

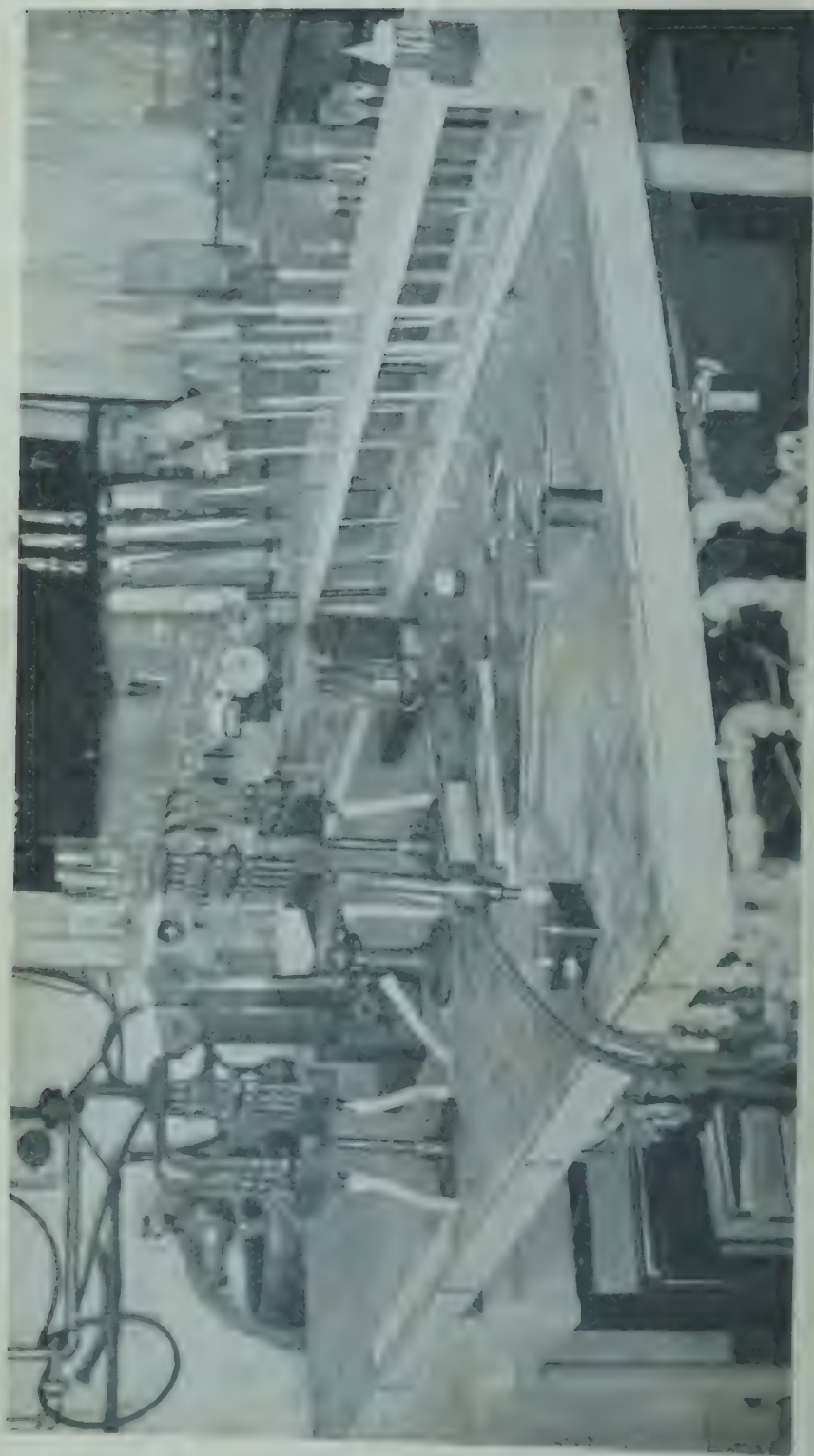
INTRODUCTION

IN the past decade the task of baking glass equipment for use in a modern research laboratory has become increasingly important. The perfection of certain types of glasses has augmented a general demand for glassware because of the sturdy equipment that could be made to withstand general usage in the laboratory. The scientist, especially the chemist, has become dependent upon glass as one of the chief materials for the fabrication of containers in which his studies are made. The advantage of observing the action of various chemical reagents under various temperature and pressure conditions has been invaluable to the research chemist. In general he has also found that some glasses are relatively inert toward chemical reagents and equipment made of these glasses could be used many times. Because the scientist has come to rely on glass equipment, the art of making specialized scientific glassware has become a distinct department in the profession commonly called *glass blowing*.

The term "glass blower" has a broad meaning and usually brings to mind the person who at various demonstrations makes artistic articles with the dexterity that often seems uncanny to the layman. Manual production of glass articles by the use of large blowpipes is also called glass blowing. A comparatively small group of persons, however, have developed the techniques of making equipment for research laboratories and it is to this group that the research chemist is greatly indebted.

Many research laboratories do not have a sufficient number of glass blowers and to carry on their work, numerous scientists have found it necessary to do a great deal of the simpler glass operations themselves. The skills they acquire are usually obtained by courses in glass blowing or by individual practice. It is for this group that the basic principles which are later outlined will be helpful in learning to do a good job of glass blowing.

The glass blower who makes the equipment for the present-day scientist is one who has spent many hours in developing the skills and techniques necessary for this kind of work. His job is more difficult than the various special crafts of forming and making equipment from metals or plastics because a great deal of his work must be completed by hand-working the glass. He has found the burner used in heating the glass as the most dependent tool. The adjustment of this burner to give flame temperatures representa-



tive of the gas that is used as fuel is one of the basic techniques to be learned.

The choice of the gases which are to be used in the burner is dependent on the type of glass to be worked. Natural gas when used with air will permit the working of lime glass or what is commonly known as a type of soft glass. The addition of a small amount of hydrogen to the air gives a slightly higher flame temperature. The substitution of oxygen instead of air gives a flame temperature which is ordinarily used in working Pyrex* (the Corning Glass Works trade name of one of the most commonly used glasses in the research laboratory). Hydrogen and oxygen, when used in the ratio of two volumes of the former and one part of the latter, give a very hot flame conveniently used in working vitreous silica or glasses with a very high

TABLE 1. Commercial Fuel Gases

Gas	B.T.U. per Cubic Foot	Volume Percent			
		H ₂	CO	Methane Plus Ethane	Propane and Butanes
Coal Gas	527	58	6	27	0
Natural Gas	1100	0	0.1	89	2
Bottled Gas	3037	0	0	0	100

silicon content. Oxygen and acetylene are also used in working these types of glasses. The average heating values and compositions of some commercial fuels are given in Table 1.

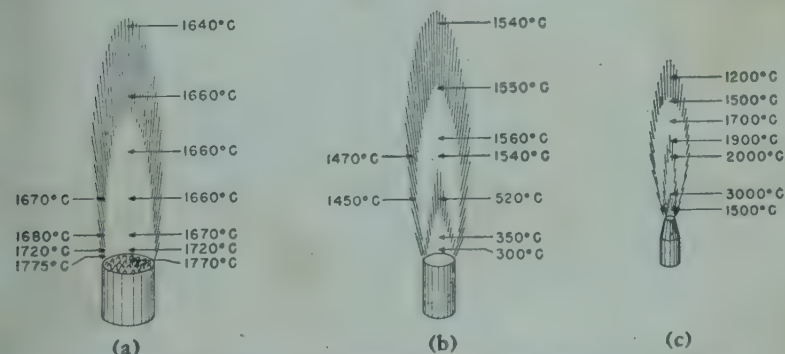


Fig. 1. The temperature distribution in the flames of (a) Meker, (b) Bunsen, and (c) the acetylene torch. After F. Haber.

The temperature distribution in the flames of blast burners is usually dependent upon the rate of combustion and the gases used. The temperature distribution in the flames of the Meker and Bunsen burners in which gas is used

The trademark Pyrex, used in this book, refers to the borosilicate glasses made by Corning Glass Works and is listed under their code number 774. The other code numbers (unless otherwise specified) are also those of Corning Glass Works.

with air is given in Fig. 1a and 1b, while that of an acetylene torch is given in Fig. 1c.

THE GLASS SHOP

The plan for the glass shop should be carefully considered. The work table is most conveniently placed so that the glass blower has sufficient room on at least two sides for freedom of movement when long sections of tubing are handled. A surrounding free space of at least four feet is adequate. Since the table is to serve as a work bench, all utilities such as gas, oxygen, vacuum and air are located under the edge of the table within easy reach of the worker and preferably

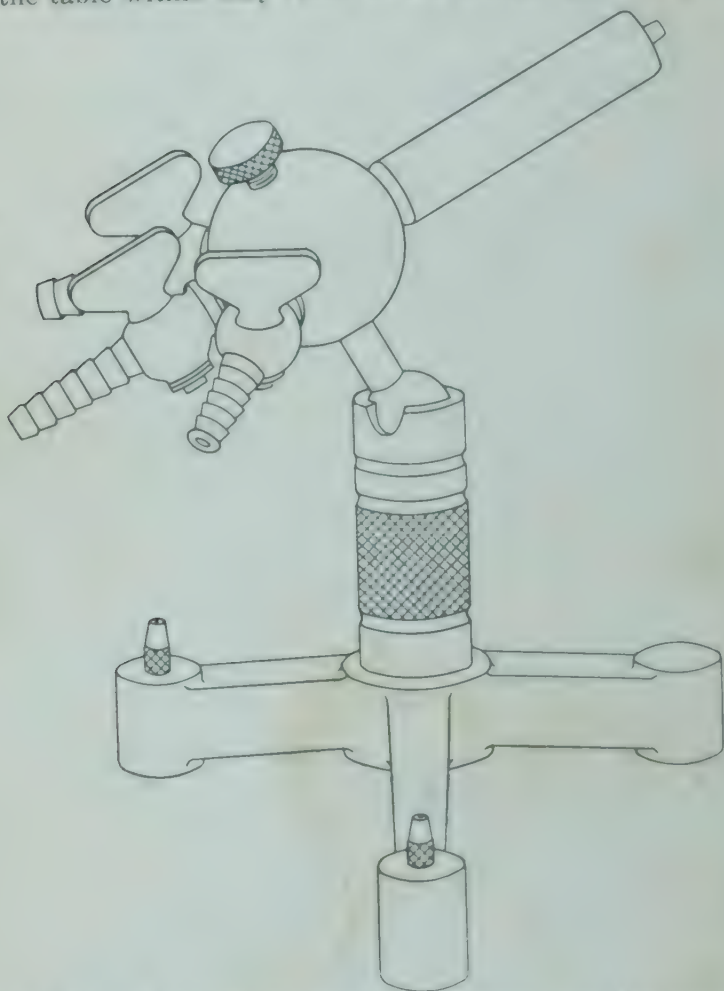


Fig. 3A. The Massachusetts Institute of Technology type blast burner close to the location of the various burners. The respective manifolds should be fitted with needle valves for precise control.

A table of about 6 to 8 ft. in length and 3 ft. in width is satisfactory. A height of 38" is suitable for the average

person. Transite about $\frac{3}{8}$ " thick will protect the table top from heat and hot glass. Special burners as cross fires will require slots in the table top for adjustment. A wooden rack with holes of different sizes is convenient as a holder for glass, tools and stems. A suitable table-top arrangement is shown in Fig. 2. The table shown here is supported by 2" standard pipe joined with crosses and tees.

BURNERS

Blast Burners: The burner of the Massachusetts Institute of Technology type, Fig. 3A, is first in the order of importance in discussing glass blowing fires. This single jet blast burner is connected to the gas and oxygen or air lines



Fig. 3B. Combination burner with two types of flames. This burner is very useful to the more skilled glass blower.

by rubber tubing of sufficient length to allow movement of the burner to any position of the working space on the table. Three interchangeable jets provide a wide range in flame size. The burner is best adapted for small work and all side arm seals.

Air is used with gas in this burner for all soft glass work. However, an oxygen and gas mixture is suitable for soft glass work if a small quiet flame is used. When laboratory resistant glass such as Pyrex is being worked, an oxygen

and gas mixture must be used. The oxygen jet should extend $\frac{1}{8}$ " beyond the outer shell for a minimum flame width. Oxygen and gas flow should be regulated until the combustion becomes slightly noisy.

The two types of flames are: surface combustion and pre-mixed oxygen and gas. The surface combustion feature provides the brush flame while the pre-mixture produces the needle point working flame.

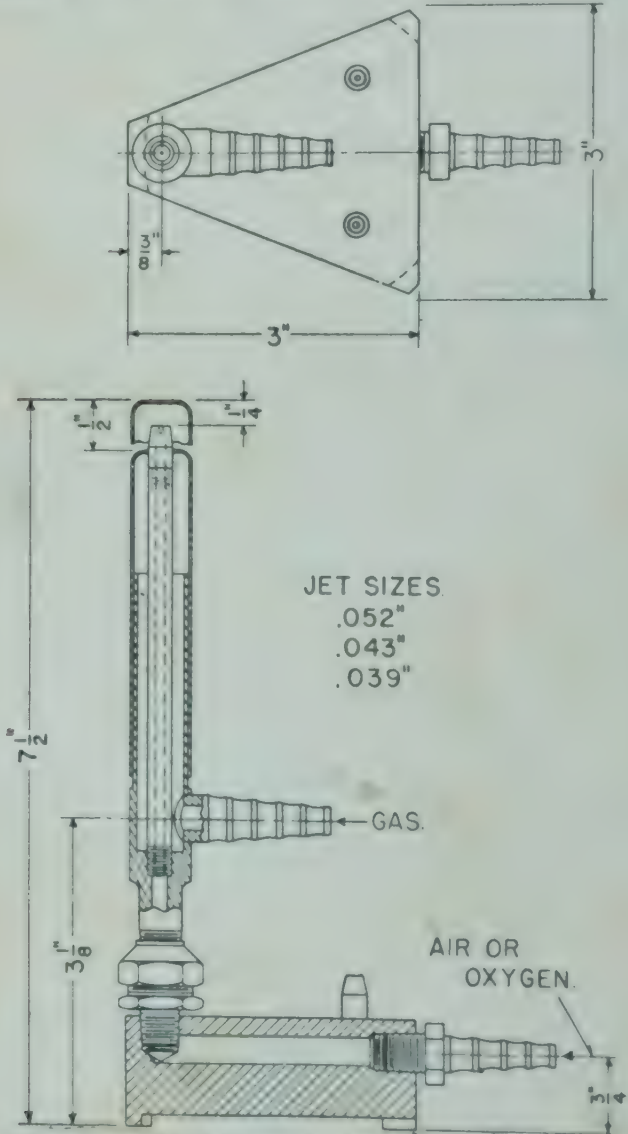


Fig. 4. Special bench burner developed by one of the authors.

The burner shown in Fig. 3B burns quietly regardless of the type of flame required, and is adjustable from a sharp needle point flame to a large brushy annealing flame.

For large side seals it is advisable to use a combination of both flames directed to a common point.

This burner was designed to operate from needle valves located on the glass blowers bench. Such a burner can be purchased from Central Scientific Company of Chicago. Their burner is mounted on a wider base and the four valves are connected directly to the burner.

A special bench burner developed by one of the authors is shown in Fig. 4. Critical dimensions are given. The base is shaped as shown to allow one to place the burner close to the edge of the table for side arm work as well as close



Fig. 5. Cross fires having glass jets, which direct an air stream through a flame.

to glass tube supporting rollers. A ball joint at the base of the nozzle allows movement in any direction or angle. Regulation of gas and oxygen or air flow is controlled by needle valves in the respective manifolds below the edge of the table. The bore sizes for the three jets are given in Fig. 4.

CROSS FIRES

Many types of cross fires are now available, but the laboratory glass shop needs, in general, are met by just four types. The fuel control and temperature attained depend on tubing size and glass compositions being worked.

Glass Jet Cross Fires. Cross fires having glass jets which direct an air stream through a gas flame are ideal for small equipment made of lime or soft glass, Fig. 5. The four jets in each bank of burners are made by drawing 13 mm. tubing down to a small capillary bore. These jets are measured conveniently by inserting a small steel needle into the bore

and cutting the tip to conform to the same diameter indicated by the needle test. The tips are not fire polished because of the danger of changing the bore size.

The adjustment of this cross fire is important. Each burner in the bank is lined to converge all flames at the center between the two banks of burners. The glass tips are projected into the gas flame $\frac{3}{8}$ ". When properly adjusted all flames will converge in the center and appear to fan out in a plane of 90° to the plane of the jets insuring a narrow working range. Should it be necessary to fabricate micro equipment with Pyrex-brand glass, the glass jets can be replaced with fused quartz jets permitting the use of oxygen instead of air.

Tubular Jet Cross Fires. The tubular jet cross fire is



Fig. 6. Tubular jet cross fires.

best suited for work in which the prime requisite is a fixed, nonadjustable flame. This cross fire with 2 to 12 jets on each side may be procured with gas valves on each jet. It is commonly used on automatic sealing machines and is shown in Fig. 6.

Laboratory Cross Fire. A cross fire developed by one of the authors for laboratory work is shown in Fig. 7. It is an adaption of the Massachusetts Institute of Technology blast burner modified to converge flames more suitably to cross flames. Unnecessary metal has been eliminated and general overall dimensions are supplied.

This versatile cross fire meets all the requirements in the manual handling of glass. Tubing up to 51 mm. in diameter is conveniently worked by using only the 2 center jets on each side. When larger tubing with diameters from 51 to 100 mm. is being worked, it is necessary to use all jets on both sides. More even heating is also obtained if a single

jet blast burner is placed directly below the point of cross fire flame convergence.

The Oxygen and Gas Cross Fire. The oxygen and gas burner shown in Fig. 8 provides a very hot flame which is excellent for working Pyrex glass. A mixer and flash stop

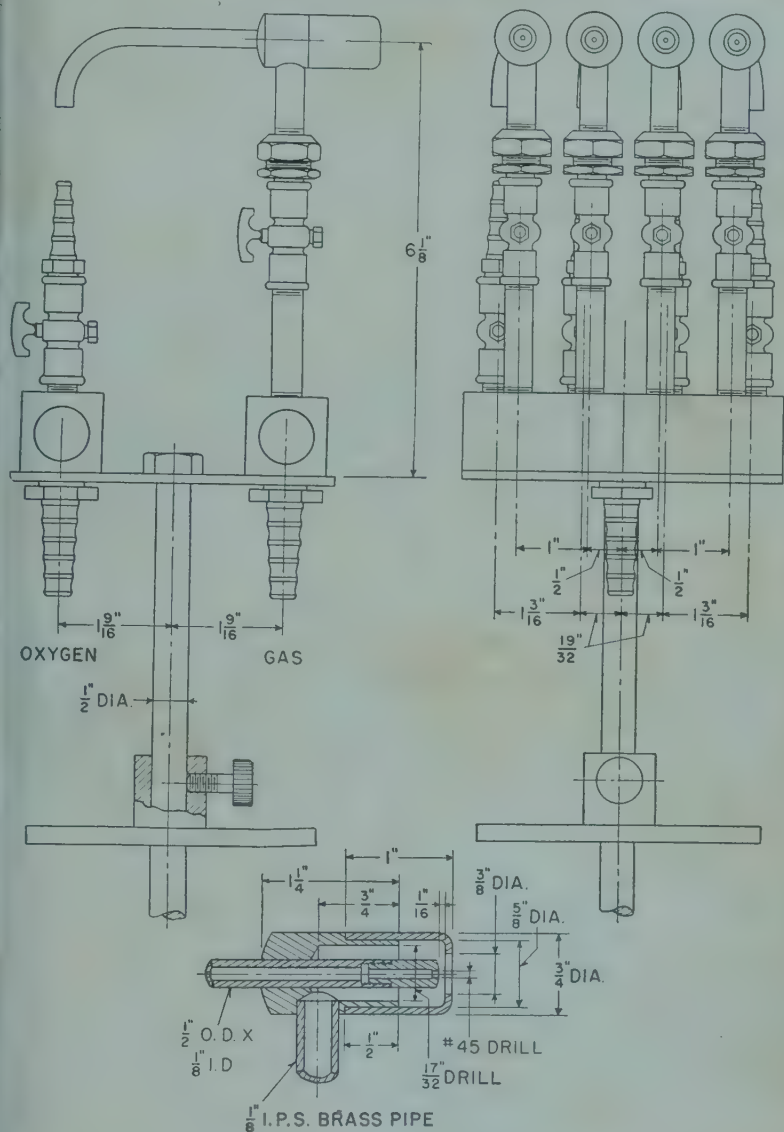


Fig. 7. Laboratory cross fire.

device are necessary on this type of burner. If machine shop facilities are not available, this type of burner can be purchased from manufacturers of glass working apparatus.

Economizer Valve. An economizer shown in Fig. 9 should always be used with cross fires because at times it is nec-

essary to shut down the working fire to allow centering and adjusting of the glass being worked. The economizer is essentially a rotary slide valve and is conveniently operated by a foot treadle permitting the use of both hands in handling or rotating the glass.



Fig. 8. The oxygen and gas burner which provides a very hot flame.

HAND TORCHES

Hand torches are very useful when glass systems are being assembled. In this work many seals have to be made in very close quarters prohibiting the use of the blast burner because of its size. Hand torches also are more conveniently used in tip-off work of small tubulations on large vacuum

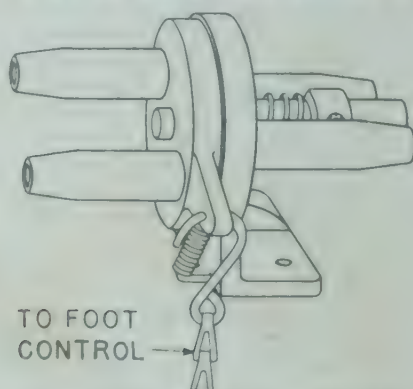


Fig. 9. Economizer valve for use with cross fires.

jackets. Three torches will suffice for all the general work in the glass shop.

Hoke Jewel Torch. Small work, particularly capillary seals are best made with this torch. Interchangeable tips

for different flame sizes are usually supplied with the torch. It is also useful in brazing and silver solder work. The torch is shown in Fig. 10.

Litton Hand Torch. The Litton torch has a swivel head and is shown in Fig. 11. It allows close working in making system seals. Higher temperatures for larger seals are obtained with a multiple head torch made by the same manufacturer.

Oxy-Acetylene Torch. Vitreous silica can be handled like ordinary laboratory resistant glass to a reasonable extent

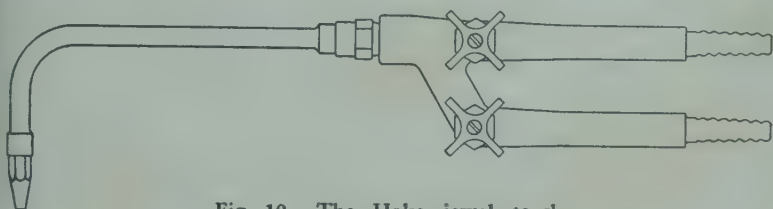


Fig. 10. The Hoke jewel torch.

with the oxy-acetylene torch. Numerous types of good torches are available. About 6 different tip sizes are necessary. This torch can be mounted by suitable clamps when a stationary flame is required.

RIBBON FIRE BURNERS

The glass blower frequently must make large sweeping bends and, although a large flame in the blast burner can

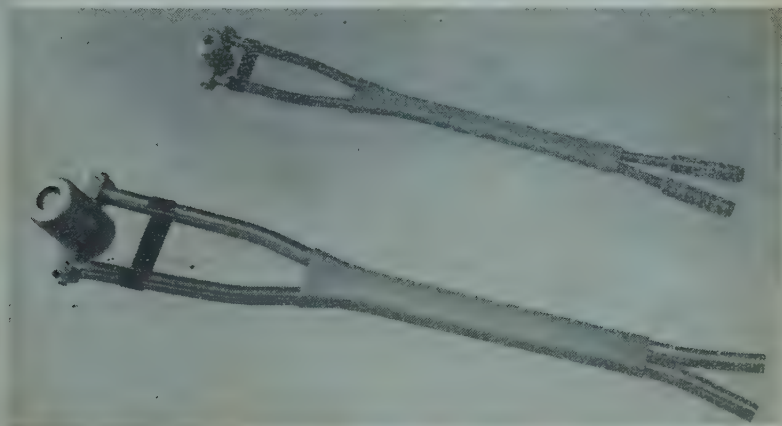


Fig. 11. Litton hand torches with swivel head permitting close working in making system seals.

be used, these bends are more conveniently made with the ribbon flame. A slide on the burner, shown in Fig. 12, permits adjustment of flame width from a fraction of an inch to the overall width up to 18 inches. This burner is particularly useful to the "sign bender."

THE ANNEALING AND PREHEATING BURNERS

Annealing Burner. The annealing of glass in a flame is one of the necessary and important duties of a successful glass blower. Numerous strains result in working glass especially when ring seals and connections are made very close together. It is essential from a standpoint of durability that the strains are reduced in magnitude. A good annealing burner is thus an important tool in the routine of working glass.

The annealing burner shown in Fig. 13 will furnish a large bushy flame for uniform heating. Two brass tubes are silver soldered to a common base and act as large jets. Although sufficiently high temperatures for average work

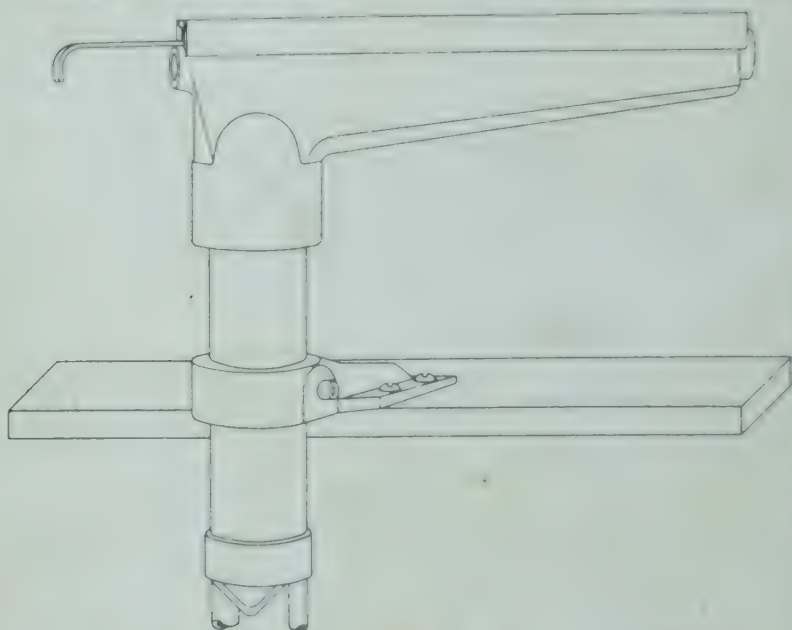


Fig. 12. Ribbon flame burner with slide which permits adjustment of flame width.

are obtained by air and gas, the temperature range may be extended by bleeding oxygen into the air line. The burner should be fitted with globe valves which allow instant opening for rapid heating to prevent cracking while transferring glass from blast burner to the annealing flame. Location of the annealer within reach of the blast burner or cross fires also minimizes loss of heat in the transfer of glass to be annealed.

Preheating Burner. The circular flame of a shielded Argand burner is excellent for preheating or maintaining near working temperatures of complex seals which are to be sealed to other glass sections. The location of this burner should be within easy reach but preferably at the rear of

the table. A small forked support near the burner will help in holding the glass which is being heated. This burner is shown in Fig. 14.

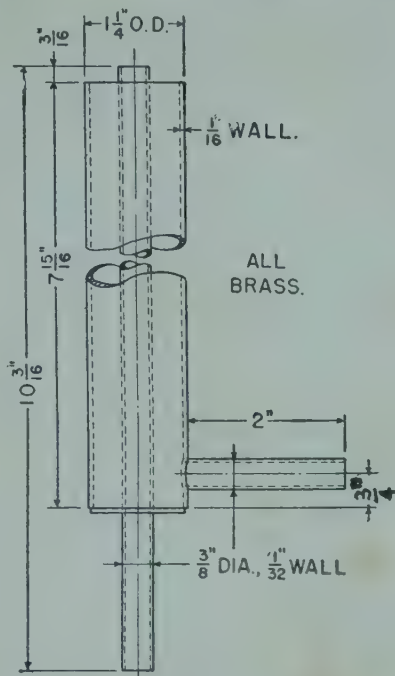


Fig. 13. Annealing burner which furnishes large bushy flame for uniform heating.

GLASS WORKING TOOLS

Although many tools may be used in working glass while it is being shaped or joined, five tools are sufficient for basic work.

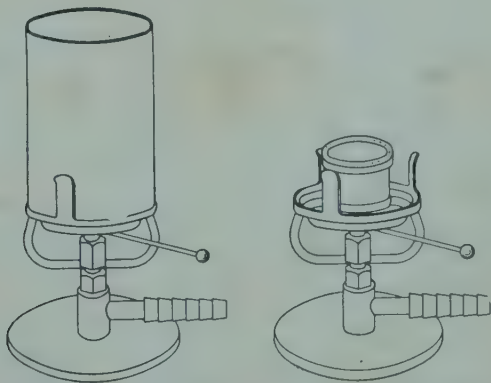


Fig. 14. Argand burner with shield at left, and at right, without shield.

Forceps. A balanced steel forceps with an overall length of 10" is shown in Fig. 15a. Transite handles serve as durable insulation.

Shaping Tools. Two shaping tools with round Transite handles are shown in Fig. 15b. The shaping ends are made of graphite.

Flaring Tools. Two flaring tools are shown in Fig. 15c. The small flaring tool is made of brass with a Transite handle. Beeswax should always be used on the metal flaring tool to prevent adherence of glass. The larger flaring tool is graphite with a Transite handle.

Blowing Tubes. The glass worker frequently has to blow glass; in fact he has found that by repeated collapsing and expanding of fused glass more durable seals can be made. Such a procedure also tends to give even thickness of glass. To permit blowing, several tubes should be made consisting of a glass mouthpiece, rubber tubing of sufficient length

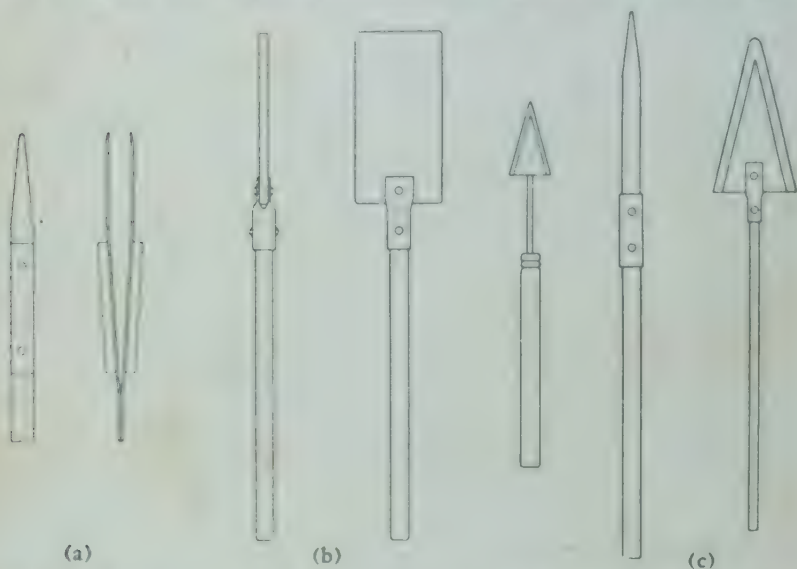


Fig. 15. Glass working tools; (a) forceps, (b) shaping tools, (c) flaring tools

and a swivel. The swivels, fabricated from aluminum, permit rotation of the glass without twisting the rubber tubing leading to the mouthpiece. Two different swivels are desirable and are shown in Fig. 16.

Adjustable Rollers. Long and heavy tubing is more easily worked by using adjustable rollers which permit rotation of the glass in the blast burner or cross fire flame with a minimum effort on the part of the glass worker. The set of rollers shown in Fig. 17 utilizes an extension for perfect and rigid alignment, eliminating the necessity of two sets. This double roller is mounted on a heavy base to minimize shifting tendencies while in use. The rolling surfaces which contact the glass are fabricated from Transite and are adjustable to various tube sizes. Critical dimensions are given in the drawing.

GLASS COMPOSITIONS

The glass blower and the scientist alike should be familiar with the physical and chemical properties of glass. Several books and numerous articles have been published in which studies of various glasses are given. The book "Properties of Glass" by George W. Morey¹ is especially recommended.

The trend in research toward finding a perfect glass has been promising in the last thirty years. Pyrex-brand glass first appeared in 1915 as a product of the Corning Glass Works and is almost exclusively used at present in the fab-

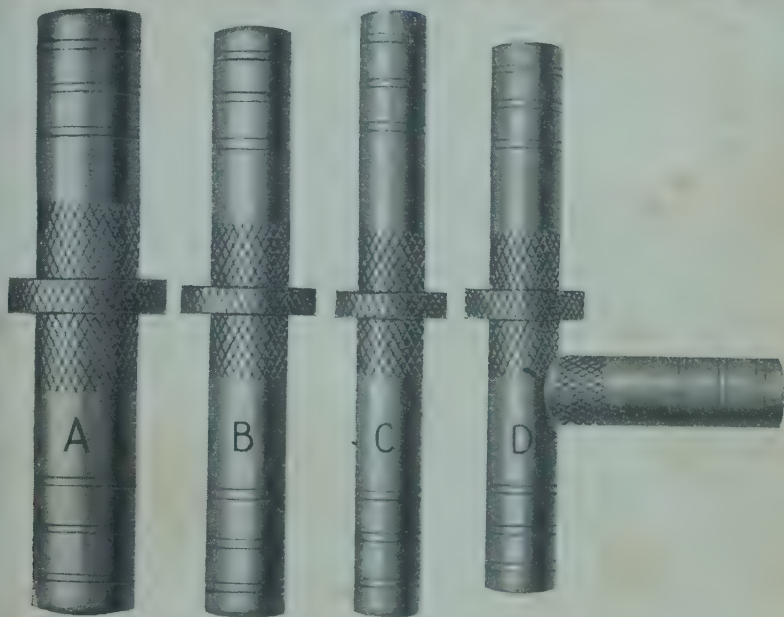


Fig. 16. Swivels to permit rotation of the glass when blowing without twisting the rubber tubing. (Photograph courtesy of Eisler Engineering Co.)

rication of equipment for the laboratory. In 1939 H. P. Hood and M. E. Nordberg of Corning Glass Works developed a process in which a glass of 96% silica content is made. This glass is comparable to vitreous silica in withstanding extreme thermal shock and with its higher softening point has given the scientist an additional durable glass for scientific equipment where relatively high temperatures are used.

Glass, according to Morey¹, is defined as follows: "A glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance, but which, as a result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid." In this definition it is inferred that glass has no definite solidification or freezing

¹Morey, G. W., "The Properties of Glass," Reinhold Publishing Corp., New York, 1938, Chapter I, page 32.

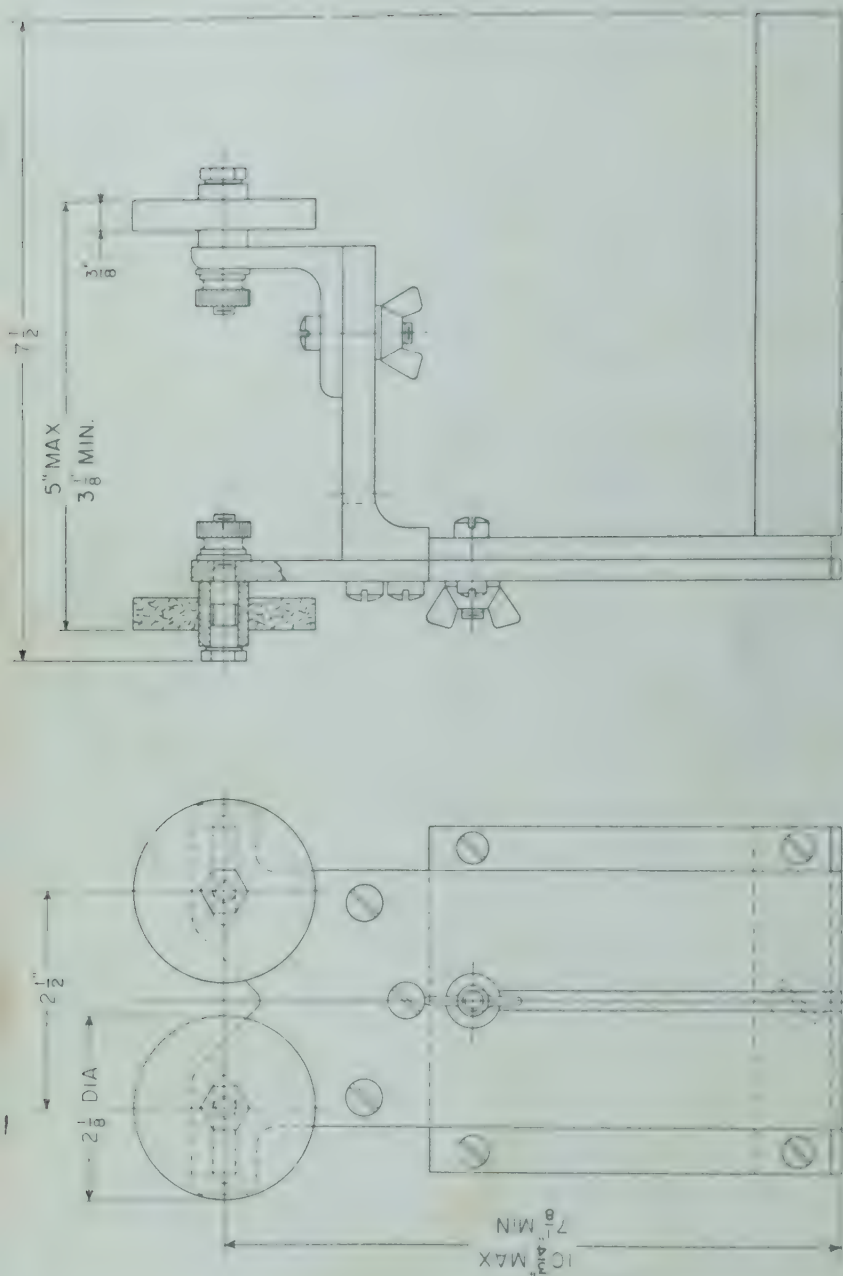


Fig. 17a. Adjustable rollers used for working long and heavy tubing.

point, but has attained solid characteristics through a tremendous increase in viscosity and not through the process of crystal formation.

Glass compounding is best understood by phase equilibrium studies of the numerous systems of glass-forming components. Certain combinations of inorganic compounds have been found to give good laboratory glasses and only through a thorough study of the phase relationships at various temperatures can one become familiar with the phase changes to be expected in working the glass. It will suffice here to mention some of the more important glass-forming compounds and to briefly point out the advantages in using some of them in compounding glass.

The most important inorganic compounds in making laboratory glasses are the oxides of silicon, boron, aluminum,

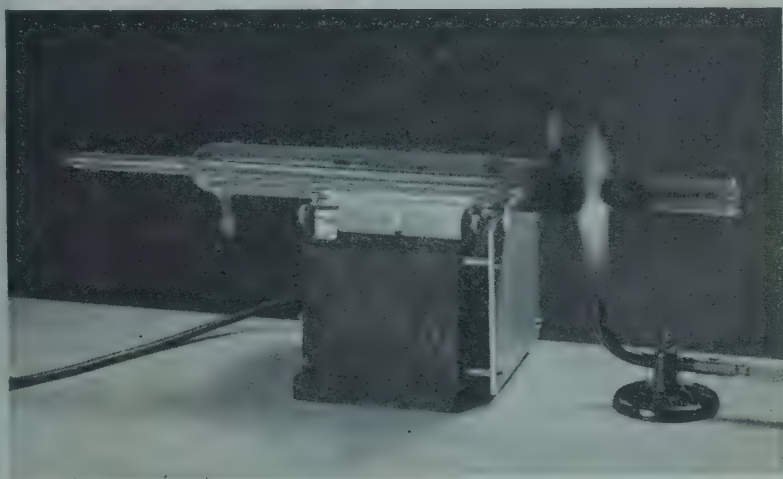


Fig. 17b. Electrically driven rollers for even and uniform heating.
(Photograph courtesy of Fisher Scientific Co.)

sodium, potassium, calcium, magnesium, lead, barium, zinc and iron. Silicon dioxide (SiO_2) is the basic component in nearly all laboratory glass ranging from 65% to 100% of the total glass. Because of the high melting temperature of silica ($1710^\circ\text{C}.$) it has been found advantageous to add oxides of boron, aluminum, sodium and potassium to lower the liquidus temperature, a temperature above which no crystallization can take place. However, the addition of the latter two oxides has a tendency of increasing the coefficient of expansion and glasses containing large amounts of these substances are also subject to attack by water and acids. It has been found advantageous to use only small amounts of the oxides of sodium and potassium. Alumina in a small quantity gives the glass a greater chemical stability and lowers the coefficient of expansion.

The compositions of various laboratory and resistant glasses according to Morey¹ are given in Table 2. It is interesting to note that the development of laboratory glass is shown in this table and that all glasses contain numerous components. Pyrex-brand glass which is most widely used in the laboratory is characterized by a very high silicon dioxide content, and yet it has the lowest liquidus temperature of any glass having such a high content of this oxide. It is because of this fact that the glass blower has very little devitrification trouble in working Pyrex-brand glass.

Lime-soda glass is still used in many types of graduate vessels. Equipment which is subjected to thermal shock should not be made of this type glass. The chemical stability also is not as good as that of Pyrex-brand glass. It is more convenient to use the same type of glass in laboratory equipment especially when graduated vessels are sealed to glass assemblies. Because Pyrex-brand glass offers more durability, it is recommended over lime-soda glass. Simpler pieces of apparatus may be constructed of the latter type

TABLE 2.

Compositions of Some Laboratory and Resistant Glasses

No.	SiO ₂	B ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	ZnO	Al ₂ O ₃	Fe ₂ O ₃
1	77.0		5.0	7.7		10.3			
2	79.4		6.4	6.7		7.6			
3	75.9		7.1	7.9	0.17	8.7		0.14	0.08
4	66.4	4.0	15.6		5.2		6.2	2.4	
5	64.7	10.9	7.5	0.37	0.21	0.63	10.9	4.2	0.25
6	73.0	3.6	10.8	0.30	4.3	0.66	5.6	1.0	0.35
7	67.3	6.2	10.9	0.30	3.4	0.79	7.8	2.5	0.23
8	66.80	4.13	7.40	1.75	2.60	1.73	9.75	2.54	0.17
9	75.90		7.29	7.84	0.15	8.73		0.24	0.10
10	76.20		7.07	7.62		8.97		0.30	0.14
11	74.32		17.56	1.38	0.11	3.67		2.35	0.14
12	77.9	14.1	4.1	2.3		0.8		0.8	
13	81.5	11.0	3.7	0.9		0.3		2.8	
14	81.4	10.6	4.4	1.1		0.7		2.0	
15	75.3	15.8	3.4	1.0		1.3		2.5	
16	75.4	17.5	3.6	0.4		0.1		1.6	
17	75.3	7.6	5.7	0.8		1.1		6.2	
18	57.4	23.6	1.9	0.5	8.7	4.7		3.2	
19	75.6	14.3	3.3	0.4		0.1		5.6	
20	80.5	12.9	3.8	0.4				2.2	

1. Stas' apparatus glass. Glass No. 73, D. E. Sharp, *Industrial & Engineering Chemistry*, Vol. 25, 1933, page 755.
2. Kavalier glass, 1879. Glass No. 74, D. E. Sharp, *Industrial & Engineering Chemistry*, Vol. 25, 1933, page 755.
3. Kavalier beaker. P. H. Walker and F. W. Smither, Technical Paper No. 107, National Bureau of Standards, 1918. Also contains MnO, 0.02; P₂O₅, 0.03; SO₃, 0.20; As₂O₅, trace.
4. Jena Gerate, prior to 1910. Glass No. 75, D. E. Sharp, *Industrial & Engineering Chemistry*, Vol. 25, 1933, page 755.

5. Jena Gerate beaker. P. H. Walker and F. W. Smither, Technical Paper No. 107, National Bureau of Standards, 1918. Also contains MnO , 0.01; As_2O_5 , 0.14.
6. Macbeth-Evans beaker, 1918. P. H. Walker and F. W. Smither, Technical Paper No. 107, National Bureau of Standards, 1918. Also contains MnO , 0.02; SO_3 , 0.02; As_2O_5 , 0.02; Sb_2O_3 , 0.60.
7. Nonsol beaker, 1918. P. H. Walker and F. W. Smither, Technical Paper No. 107, National Bureau of Standards, 1918. Also contains MnO , 0.01; Sb_2O_3 , 0.62.
8. Kohln-Ehrenfeld. J. D. Cauwood and W. E. S. Turner, *Journal Society Glass Technology*, Vol. 2, 1918, page 219. Also contains As_2O_3 , 2.05; Sb_2O_3 , 1.29.
9. Resistance, "R." J. D. Cauwood and W. E. S. Turner, *Journal Society Glass Technology*, Vol. 2, 1918, page 219. Also contains As_2O_3 , trace; MnO , 0.13.
10. Zsolna. J. D. Cauwood and W. E. S. Turner, *Journal Society Glass Technology*, Vol. 2, 1918, page 219. Also contains Sb_2O_3 , 0.30.
11. Japanese. J. D. Cauwood and W. E. S. Turner, *Journal Society Glass Technology*, Vol. 2, 1918, page 219. Also contains MnO , 0.10.
12. Silex. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193.
13. Vulkanite. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193.
14. Resista, 1923. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193.
15. Resista, 1925. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193.
16. Tempax. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193. Also contains Sb_2O_3 , 1.6.
17. Jena Gerate, 1920. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193. Also contains BaO , 3.5.
18. Jena Supremax, 1565^{III}. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193.
19. Jena Durax 3817^{III}. H. Thiene, *Zeitschrift fuer angewandte Chemie*, Vol. 39, 1926, page 193. Also contains Sb_2O_3 , 0.4.
20. Pyrex chemical resistant glass.

glass and if a supply of oxygen is not available, it is necessary to use this glass because it can be readily worked with air and gas.

Lead glass is being used extensively in rare gas tubes and fluorescent lighting. It is particularly useful in the glass-to-metal seals required in their construction. This type of glass is easily scratched and is attacked by a number of chemical reagents. In working lead glass a stronger oxidizing flame is recommended; otherwise reduced lead will blacken the seals. Seals started in tubing with blackened edges will leak and no amount of working eliminates the lead. A slight darkening on the outside will disappear if the glass is held in the tip of a flame containing an excess of air.

Vycor-brand glass which contains 96% silica with boric oxide and traces of the oxides of aluminum and iron as the remaining ingredients is produced by the specialized leaching process by Corning Glass Works. It is marketed under

their code numbers of 790 and 792. The former is transparent and can be used up to a temperature of 900°C . The 96% silica glass 792 is translucent and can be used to a temperature service limit of 800°C . Both glasses have a low linear coefficient of expansion and have softening points at about 1500°C .

The chemical resistant glass known under the trade name of Pyrex is used extensively for a general all-purpose glass in the laboratory. As was shown in Table 2 it is a borosilicate glass having a low potassium and sodium oxide content. This glass is listed under the Corning Glass Works Number of 774, has a softening point of 820°C . and can safely be used in repeated heating operations up to 600°C . Its linear coefficient of expansion is four times that of Vycor-brand glass.

An alkali resistant glass known as "Corning" 728 which is boron-free is used when resistance toward alkalies is desirable. This glass has a linear coefficient of nearly twice that of Pyrex-brand glass and consequently should not be used when resistance toward thermal shock is desired. This glass has a softening point of about 870°C .

PROPERTIES OF GLASS.

The glass blower must be familiar with the coefficient of expansion of various glasses. All glasses are poor conductors of heat and require gradual heating and cooling, especially when equipment with complex seals is changed or repaired. Rapid heating of seals will cause breakage and the beginner must be aware of this fact.

In the construction and repair of laboratory apparatus it is necessary to use tubing with the same physical characteristics as the glass from which the apparatus was originally made; otherwise, unnecessary strains due to uneven expansion may cause subsequent breakage. The low thermal expansion coefficient of Pyrex-brand glass permits heavy and rugged construction thereby increasing the resistance to mechanical breakage. This glass is well within our working range and is used extensively for laboratory apparatus. Contrary to popular belief, the manipulation is less difficult than soft glass if provision is made for efficient burners. It would be

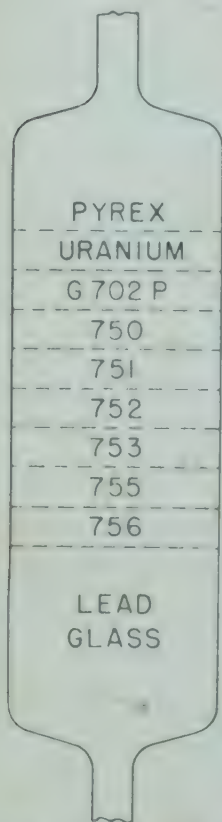


Fig. 18. Series of glasses for sealing lead glass to Pyrex.

impossible to duplicate the more complicated equipment which is now made of Pyrex-brand glass by substituting soft glass, and furthermore, the apparatus would fail under conditions which are imposed upon it.

The glass blower must also have information about the coefficient of expansion of the glasses when he is required to seal two different types together. As an example, suppose a certain piece of equipment of lead glass is to be sealed to Pyrex. It would be impossible to seal the two directly together; instead, a series of thin and well annealed seals are made in the order shown in Fig. 18. Here the coefficient of expansion of each glass, for which the code number of the Corning Glass Works is given, range in respective order between that of lead glass and Pyrex.

A comparison of the relative linear coefficient of expansion of several glasses is given in Fig. 19. The increase in length shown by the dotted portions corresponds to a

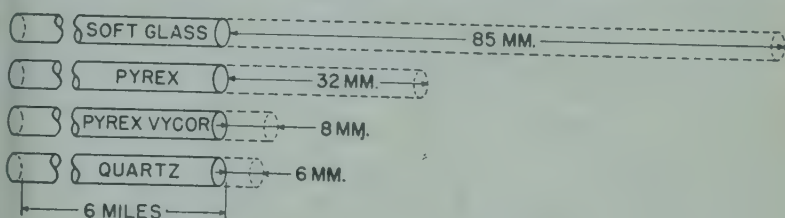


Fig. 19. Increase in length of various glasses with increase in temperature of 1°C .

temperature increase of 1°C . The coefficients of expansion, as well as the softening, annealing, and strain points of several Corning glasses are given in Table 3.²

A knowledge of the chemical durability of glasses is important when scientific equipment is made. Pyrex-brand glass or Vycor is adequate for nearly all general purposes except when strong and hot alkali solutions are continually used in the apparatus. Under such conditions "Corning" 728, an alkali resistant glass, may be advantageously used. It has been found more practical however to use Pyrex-brand glass in assemblies which are exposed to alkalies because it is often easier to replace the exposed parts than to use a different type of glass which requires graded seals in connecting it with the remainder of the assembly.

DEVITRIFICATION

Devitrification was a constant threat in the development of glass for the laboratory but by accurate compounding of glass this danger of crystal formation has been greatly eliminated. Usually when frosting of the surface appears

²Phillips, C. J., "Glass: The Miracle Maker," Pitman Publishing Corp., New York, 1941, Chapter VIII, page 183.

TABLE 3. Some Sealing Glasses Manufactured by Corning Glass Works, Corning, New York

Sealing Glass Series						
From	*Code No.	Lab. No.	Expan. $\times 10^7$	Soft. Pt. (°C)	Anneal. Pt. (°C)	To
Fused silica (15-5.8) No. 790	{ 790	790-H	8.	1510 \pm 30	890 \pm 20	No. 774
	{ 723	707-GS-1	13.5 \pm 1	1160 \pm 20	750 \pm 20	
	{ 720	707-GU-1	19. \pm 1	1125 \pm 20	645 \pm 20	
	724	715-AO	21. \pm 1	840 \pm 10	583 \pm 10	
	774	726-MX	32-33	819	553	
No. 774 Kovar } Fenico } Molybdenum	772	702-P	36	756	526	{ Tungsten (45) Kovar } Fenico } — (47)
	705	705-AJ	46	703	496	
	{ 704	705-BA	49	697	484	
	{ 706	705-AO	50	693	494	Molybdenum (53-55)
	752	750-AJ	62	747	566	
	753	805-F	70	728	557	
	755	805-G	77	716	546	G-1, G-12
	756	750-AL	85-88	702	536	
G-1 & G-12	012	G-12	87	630	431	{ Platinum (90) Nickel irons (90) Chrome irons (100) Dumet Allegheny type (110)
	001	G-1	90	626	425	
	008	G-8	92	696	510	
	025	125-AJ	98.6	648	464	

Numbers in parentheses represent approximate linear expansion/°C. $\times 10^7$.

in "Pyrex" seals, it is not the cause of the glass composition but instead the carelessness of the worker. The glass blower finds that the danger of causing devitrification is greatest when force is exerted on a seal at the time when the red glow is departing from the glass prior to annealing. Experience in working glass is the best way in learning to prevent devitrification, and the beginner may find it helpful by noting what method of handling causes frosted seals.

CUTTING GLASS

Consideration must be shown to the composition of the glass in operations which involve cutting. Some cuts made on soft glass (lead or lime-soda) would fail on Pyrex and certain techniques used on Pyrex would cause serious trouble with soft glass. Undoubtedly, the harder the glass, the more patient one must be. The difference lies in the fact that soft glass breaks too easily and especially when one tries to duplicate the diagonal and slot cuts made on Pyrex with a carborundum wheel.

Glass tubing in sizes ranging from minute capillary up to approximately 25 mm. o.d. should be scratched by an abrasive instrument and then broken apart by the use

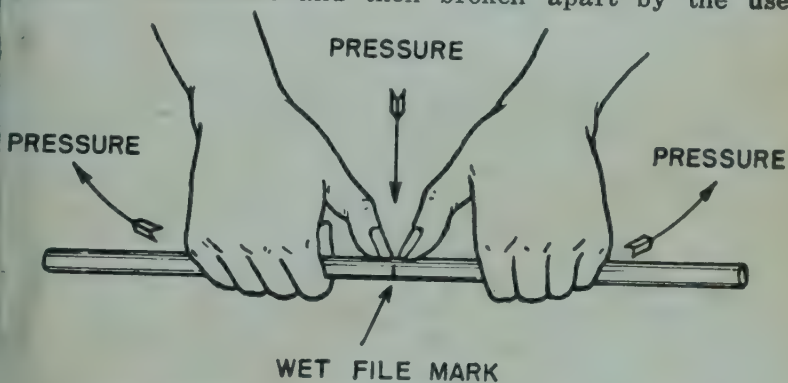


Fig. 20. Method of breaking tubing 13 mm. and smaller.

of both hands. Whether one uses a steel wheel, a glass knife or a three-cornered file, the technique is the same. The scratch is made cleanly, perpendicular to the tubing, and it is not necessary to try to saw through it. Expert flat glass cutters make only one scratch, but on tubing it is best to scratch the glass twice. If the abraded surface is wetted with water, it will break more easily. Usually glass blowers employ this trick but cannot explain why the glass is weakened. Milligan³ has shown that the tensile strength is decreased by wetting glass containing a small crack. After scratching and wetting, the thumb nails are placed against the back of the tubing for a fulcrum directly op-

³Milligan, L. H., *Journal Society Glass Technology*, Vol. 13, 1939, page 35.

posite the scratch. The break is then made by a combined bending and pulling force back and away from the mark, Fig. 20. It should be pointed out that files and cutting wheels are only effective when new and sharp, and tungsten carbide-edged knives must be resharpened continually.

For 13 to 25 mm. tubing a different hand hold is advisable. The glass tube is scratched, wetted and grasped in a full grip with a hand on each side of the mark. Each

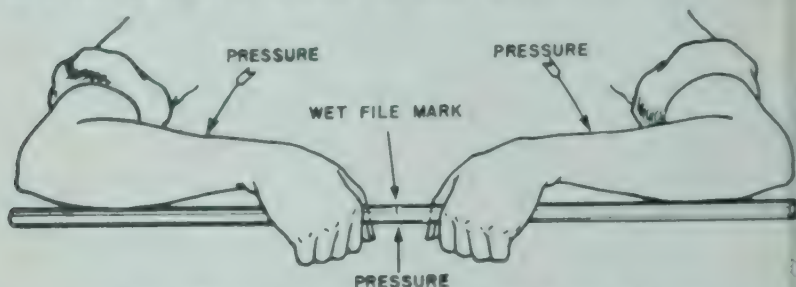


Fig. 21. Method of breaking tubing larger than 13 mm.

arm is allowed to rest against the tubing as shown in Fig. 21. The glass is then broken by pulling back and away with the arms exerting a perpendicular force to the tubing.

On a glass system where tubes are interlaced from one



Fig. 22. Electrically heated hot wire system for breaking tubing of large diameter. (Photograph courtesy of Fisher Scientific Co.)

fixed object to another, one is limited to a minimum of pulling or tugging for fear of serious breakage. This fixed tube must be marked with the edge of the file, then wetted as described before. The point of a 5 mm. glass rod is

heated white hot and touched to the center of the scratch. Generally a crack begins and encircles the glass completely. If it starts but does not run completely around the tube, then lead it by touching a hot glass rod just ahead of the crack in the proper direction until complete.

Tubing of larger diameter can be cut using the application of heat by means of a hot wire. Here the scratch must encircle the glass. A scratch made manually is often not concentric with the tube. A steel wheel with a thin sharp edge about 12" in diameter, mounted on a motor shaft, will make a perfect circle scratch when the glass tube or bulb is turned against it, provided a stop is employed at the end of the tube to prevent shifting.

An electrically heated hot wire system is illustrated in Fig. 22. A semi-loop of 26 S.W.G. nichrome wire is adjusted to the tubing diameter and arranged in series with a suitable resistance, which is encased as shown in Fig. 22, and connected to a 110 volt source. The resistance may be replaced by a variable transformer. The tubing is placed against the wire which coincides to the scratch. The current is switched on and the glass is held steady for a short length of time. On thin walled glass the crack will begin of its own accord, but on heavy walled glass it is started by touching a cold wet paper or cloth to the center of the heated portion. Once started, the crack is led by holding a new portion of the uncracked circle against the red hot wire. NEVER LEAVE A GAP between the part to be cracked and the crack already started. Soft glass should be rotated against the wire because it will crack completely around almost immediately.

A modern cutting machine is a requisite to the glass shop. A suitable cutter consists of a bonded abrasive wheel 12" in diameter and 0.04" thick which rotates with a stream of water played upon it from both sides, Fig. 23. Cuts of any angle desired can be made by a simple manipulation of a geared miter head located on the cutting table. True clean cuts can be made and in certain operations may save valuable time. A cut for example could be as small as $\frac{1}{32}$ ". By proper holding or clamping, tubing ends can be slotted. Since glass is very brittle and tubing is usually bowed slightly, care must be exercised to avoid a strain on a partially finished cut. The glass may be supported and held tight by the left hand and the right hand should lightly dampen vibration. At the completion of the cut, slower cutting will eliminate the possibility of burred edges. Observation will show a semi-polished edge, which if sealed to another tube, would leave a permanent gray line. This can partially be removed if fire polished before sealing together. If the end were reinforced by melting down a small portion of the tube and belled slightly, the cut mark would barely show. In the preparation of parts, long lengths of

tubing can be cut to lengths a little longer than desired and these may be used in such a manner that their cut ends are removed in the flame.

The wheel is powered by a $\frac{1}{2}$ horsepower motor at 1760 r.p.m. Water may be applied by a recycling pump from the water sump or straight from a water line. The table runs true, being mounted with two flat rollers on one side and two pulley wheels on the other. It moves back and forth on parallel bars. The guard is a safety device which prevents splashing.



Fig. 23. Modern cutting machine. (Photograph courtesy of American Instrument Co.)

Occasionally a cutting job is necessary on different types and sizes of large soft-glass containers. Instead of employing a scratch and hot wire system, the container is placed on a turntable which can be turned just fast enough that centrifugal force will not throw it off center. A small Hoke torch is clamped solidly in position and as the turntable is set in motion, an oxygen and gas flame is played in a set position approximately one-quarter of an inch from the glass. After a number of revolutions, the glass vessel will crack cleanly and square. This end may then be ground on a flat plate with carborundum and water, but do not attempt to fire polish the edge. The arrangement of such

a turntable is shown in Fig. 24. It should be pointed out that a procedure, as outlined here, depends upon the rapid heating of a narrow portion of the glass to cause fracture. The glass blower should remember this when he is working on a glass assembly with a hand torch. Unintentional movement of a hot flame across tube sections may cause immediate or subsequent breakage because of strains set up in the glass.

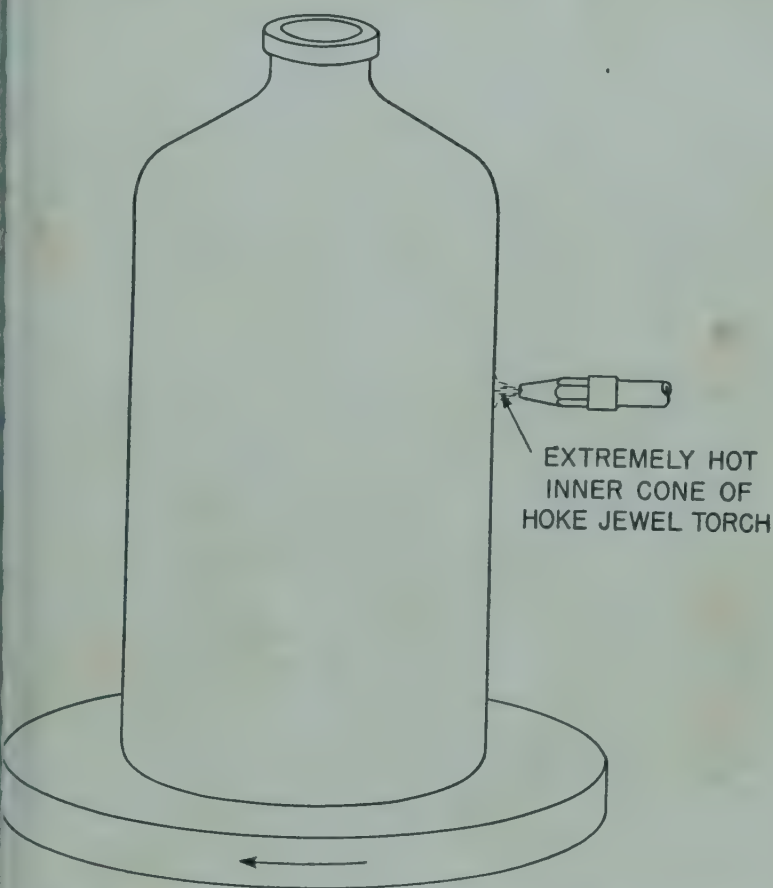


Fig. 24. Arrangement for cutting very large soft glass containers.

GLASS AND GLASS STORAGE

A prime requisite in blowing glass is that all glass be clean. A sufficient supply should be stored in a dust-proof cupboard. Tubes should always be cleaned both inside and outside before they are used. Swabs for different tube sizes are easily prepared by using a piece of folded cheesecloth tied to a stout cord.

A small weight tied to the free end of the cord will aid in dropping it through the tube. The swab is then drawn

through the tube. Cleaning solutions of sodium dichromate in sulphuric acid or solutions of commercial detergents are often required and should be prepared and stored in reagent bottles.

In the repair of broken equipment the glass blower should be sure that all surfaces are clean, especially those that must be fused in the blast burner.

CHAPTER II.

ELEMENTARY GLASS BLOWING SEALS

The fabrication of durable and perfect glass apparatus can only be assured by a complete mastery of fundamental operations. Certain techniques in handling glass are involved and if extreme care and patience are exercised in learning the basic procedures of sealing glass, no difficulty will be encountered in fabricating more complex equipment.

The beginner may find that the first problem in glass fabrication is the proper degree of fusion of the glass. Glass is essentially a super-cooled liquid and consequently does not have a definite melting point but will soften gradually and finally flow when heated in a blast burner flame. The temperature range of fusion depends on the type of glass but in general the degree of fusion required for successful fabrication of nearly all glasses is approximately the same. Glass must be fused sufficiently for correct handling. This in itself is sometimes quite a problem, for the beginner frequently does not heat the glass sufficiently for good leak-proof seals. The other extreme is that the glass is fused so much that the potential glass blower loses control over his work and his glass seals are of varying wall thickness.

The correct procedure in learning to fuse glass is to make certain that the glass is heated uniformly in the burner flame. In making seals with tubing or heating glass rods, it is necessary to rotate the glass in the hottest zone, which is at the tip of the blast burner flame. It is desirable that a minimum of glass be heated and fused in completing seals because no matter how careful a glass blower may be, it is extremely hard to make perfect seals with wall thickness identical to that of the original glass. If a large portion of the glass is deformed by partial fusion it will require more work in making smooth seals.

Three characteristics of fused glass influence successful manipulation. They are as follows:

1. *Gravity*.—Glass in a viscous state will always flow with gravity. To properly seal glass it must be continually rotated as it is being fused or it will sag and become so deformed that smooth glass seals are impossible.

2. *Surface Tension*.—Viscous glass has also a tendency to flow under the forces of surface tension. Fusion will yield rounded ends on rods, and tubes are fire-polished by

heating them sufficiently to fuse the edges. Surface tension of the fused glass will cause it to flow to give rounded ends or edges. There are, however, instances when surface tension forces are not helpful in working glass. This occurs when small sections of glass are not entirely joined in making glass seals. Fusion of these small openings will cause an enlargement of round holes; and then such holes can be closed only by pulling the fused glass together with a small glass rod. Another procedure is to deform the seal sufficiently to close the opening before work is continued in completing the seal. The latter procedure is not recommended since additional work is required in shaping the glass to form a good seal.

3. *Timing in Working Glass.*—Seals are made by working together the glass of two tube sections. This is accomplished by the process of collapsing the glass at the seal with heat and then expanding it with air pressure by blowing into the assembly. It is important that blowing out the glass is timed in such a way that when the desired wall thickness is obtained, pressure is momentarily released to allow that glass to cool just enough so that it cannot be expanded upon further blowing. Should portions of this seal still have heavy walls, they can then be blown out because the temperatures in these parts are still high enough to permit the glass to be expanded under pressure. The glass can thus be worked to a uniform wall thickness by repeated collapsing, expanding and pulling the expanded portion to the diameter of the tubing.

CHOICE OF GLASS FOR INSTRUCTION AND PRACTICE.

The choice of glass will depend on the facilities available. Lime or soft glass can be worked with gas and air. Economy is effected in using this type of glass because no oxygen is required as in the case of working Pyrex. The former type of glass is also less expensive. There is, however, little difference in the technique required for working either type of glass. As lime-soda glass has a higher coefficient of expansion; it must be heated more slowly; and if it is used in capillary tube form it must be carefully annealed. Pyrex glass has a rather low coefficient of expansion and can be heated more rapidly.

ANNEALING

The annealing of glass seals is important if durable equipment is desired. Internal strains are always developed when glass is fused and sealed and, to relieve the majority of these strains, glass must be heated to annealing temperatures. This may be accomplished by heating the glass in electrical furnaces or with annealing burners. The former

method will be described under the fabrication of more complex equipment. The latter method is best performed by heating the seal in a large gas and air flame of an annealing burner. The glass is heated until it has a dark cherry red color. Under these conditions it becomes pliable and care must be taken in the rotating movement that the glass is not forced in any way. The air is turned off and

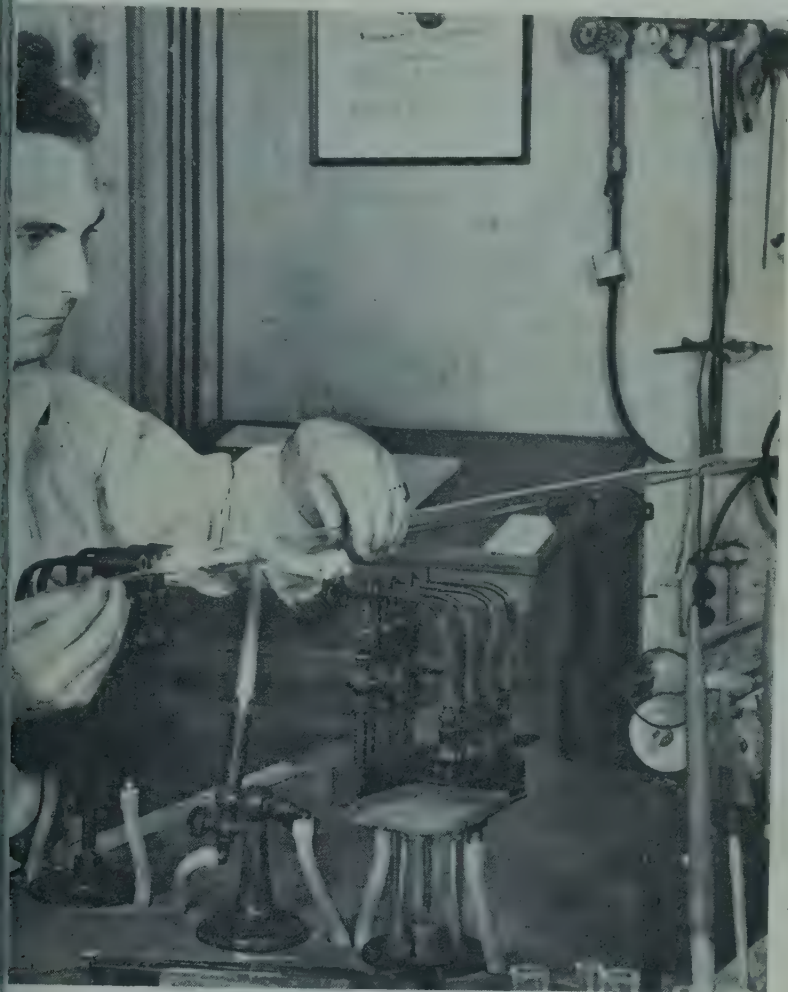


Fig. 25

he glass is coated uniformly with a thick layer of carbon.* It is then removed from the flame and allowed to cool without touching cold surfaces.

*The glass is coated uniformly with a thick layer of carbon by incomplete combustion of the gas: The deposit of carbon forms on the glass when the temperature of the glass drops to that of the gas flame. This is desirable in order to keep the outer surfaces hot and still allow the overall temperature of both inner and outer sections to drop slowly.

All seals should be annealed as soon as they are finished. This is especially important in more complex work because the seals when completed are hot and there is less danger of cracking the glass by the necessary reheating. If it is necessary to anneal the glass at a later time, it must be heated slowly to the annealing temperature by gradually increasing the gas and air to the burner. Frequently a straight gas flame is desirable during the warming period before air is added to attain the annealing temperature.

POINT PULLING

Fundamentally the basic technique in the art of fabricating glass is the proper handling of the glass while it is being fused. Small tubing can easily be handled but to relieve awkwardness in working larger tube sizes, a portion

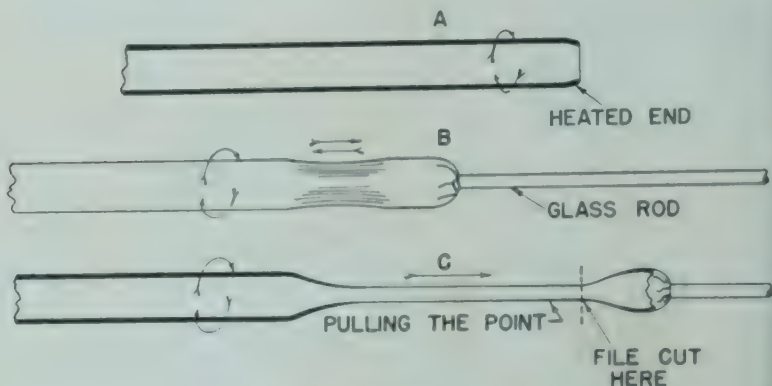


Fig. 26

of the glass is most conveniently drawn down to a long heavy-walled point. This forms an axis, about six inches in length, with which to hold and rotate the glass. In addition to being heavy enough to bear the weight of the tube, it has also to be truly coaxial with the tube to permit rotation without wobble.

The size of the point is determined by the amount of glass used. Although there is a definite increase in wall thickness with an increase in tubing diameter, the amount of glass needed for good heavy points on larger tubes must be obtained by heating a longer section of the glass.

Pulling points on glass tubing is given in three steps. The proper hand hold for point fabrication is shown in Fig. 25. The left hand, arched at the wrist, supports the main weight of the glass; the right hand supports the end of the tube. It is more economical to use glass rods about

four inches long, especially when large tubes are being worked, because it is easier to follow the rotation of the glass by turning the glass rod with the right hand. Practice in holding and rotating the glass as outlined above is required before an attempt is made in point pulling.

The tube must be perfectly balanced while it is being rotated and, when points are to be pulled on large sections or large-diameter tubing, it is better to use aligned double rollers for a support: the glass tube is pressed against the rollers and rotated with the palm of the left hand.

1. After the hand hold and the rotation of the glass has been mastered the end of the tube is fused as shown in Fig. 26A. A glass rod is then attached to the fused end and centered with the right hand while the tube is being rotated. The rod must be truly centered because the point axis will depend entirely upon the alignment of the attached rod.

2. The tube is heated at the shaded section as shown in Fig. 26B. Two distinct motions are required, tube rotation and a longitudinal movement. The latter is governed by the tubing size because more glass must be used for heavy-walled points on larger sized tubing. The glass is heated over the specified zone until it becomes uniformly dark cherry red.

3. It is then removed from the flame and drawn slowly down to a point. The dotted line in Fig. 26C indicates the position of the file cut to remove the waste glass.

Continued practice is recommended. This is accomplished by pulling successive points with bodies about two inches long on a long glass tube which is supported on rollers. Each point is used as a handle for the next one.

A second exercise which is useful in developing the technique of holding the glass in the left hand is to cut a glass tube about one inch in diameter into sections one foot in length. The sections are supported in the left hand as shown in Fig. 25 and successive points are pulled on the tube. In this case the body of the tube may be restricted to about one inch in length.

CUTTING GLASS WITH BLAST BURNER

The technique in cutting glass with a file has been described in Chapter I. In preparing tubing ends for butt seals it is advisable, however, to cut the tube with the burner flame. File marks are hard to eliminate from the glass and when seals are made with tubing containing these marks a small opaque section is always apparent in the seal. This can be eliminated to a certain extent by fusing the tube end and working the glass with a small round

or hexagonal carbon tool. The best method in preparing tubing ends is described in the following operation:

1. The section of tubing with an axial point shown in Fig. 27A is held in the left hand. The end of the tubing body is fused in a blast burner flame by uniform rotation of the tube.

2. A glass rod is attached and centered to the fused end.

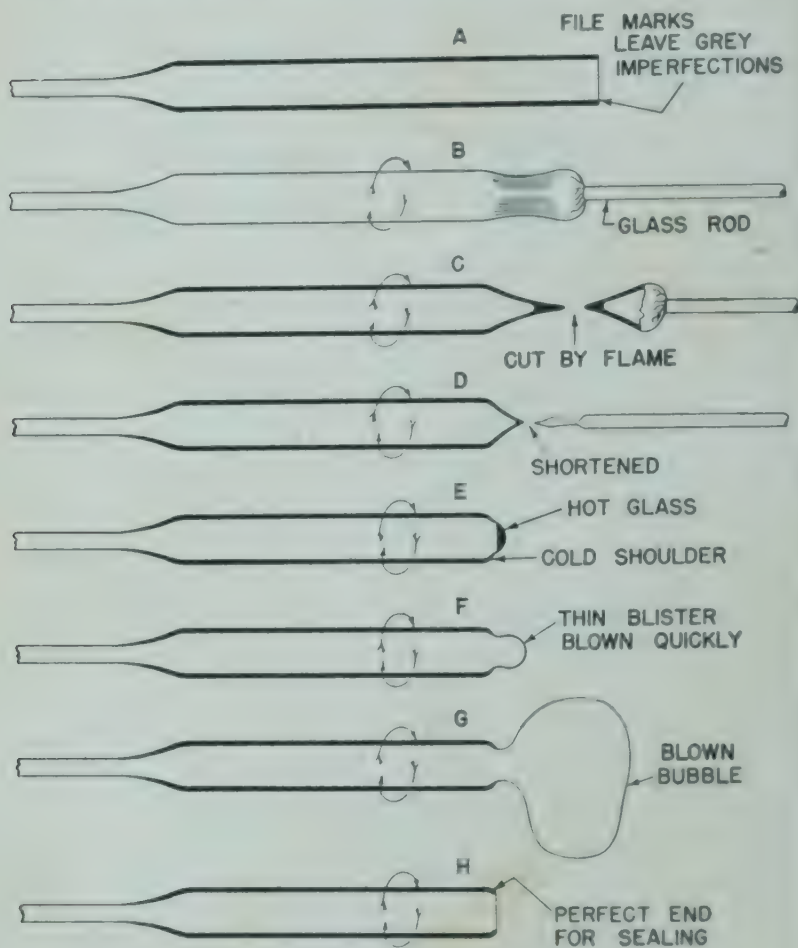


Fig. 27

The section illustrated by the shaded portion in Fig. 27B is then heated in the flame by continually rotating the glass by both the point which is held in the left hand and the rod which is held in the right hand.

3. After the glass has fused sufficiently, it is drawn apart by pulling away the portion fused to the glass rod. This operation is completed without removing the glass from

the flame. The closed end of the tube has the shape shown in Fig. 27C.

4. The slightly elongated tip is removed by again attaching the glass rod while the tube tip is rotated in the flame. The glass is then cut away by heating between the shoulder and tip of the closed tube and pulling off the excess glass with the rod as shown in Fig. 27D.

5. The tubing end is allowed to cool slightly. The tip is heated with intense heat until the fused end appears as shown in Fig. 27E. At this time the open end of the point is brought quickly to the lips. A small puff will blow the white-hot lens-shaped portion of the glass into a small bulb as shown in Fig. 27F.

6. The tube end is allowed to cool slightly and then reheated at the bulb by even and continued rotation. When the glass becomes hot the end is blown out by again blowing quickly into the open end of the point. As the bulb enlarges to a 2" diameter, air pressure is released. The form of the tubing at this stage is shown in Fig. 27G.

7. The thin bulb is then scraped away by a sidewise movement of the forceps. The rough unfinished edge is then fire polished in the flame by heating the end with even rotation until it is fused as shown in Fig. 27H.

BUTT SEALING

Regardless of tubing size, the following technique is used in sealing together glass tubing with identical diameters. A point should be drawn on the two tube sections unless the diameters are below 10 mm. Two ends are prepared as described above. The ends should be even and square with the tube. The burner is then regulated to give a narrow flame and the open end of the point, to be held in the left hand, is closed by fusion in the burner flame. All blowing operations are performed through the end of the point which is balanced and held with the fingers of the right hand. The sealing procedure is as follows:

1. Both ends to be sealed are rotated in the flame to insure even fusion around the entire circumference of the tube end as shown in Fig. 28A.

2. The tubes are contacted at an angle as shown in Fig. 28B so as to form a hinge to steady the hands while the tubes are brought into exact register and butted together.

3. The joined ends are then heated around the circumference by continued rotation. The beginner will find it difficult to synchronize the rotating motion of both hands. When a drag is noted, because the rotation of one tube is faster than the other, the direction of rotation should be reversed before the two tubes are twisted at the fused portion.

4. A constriction occurs as the glass is further heated. This is shown in Fig. 28C.

5. After the constriction becomes quite noticeable, the glass is removed from the flame and the constriction is enlarged by blowing through the open end of the point

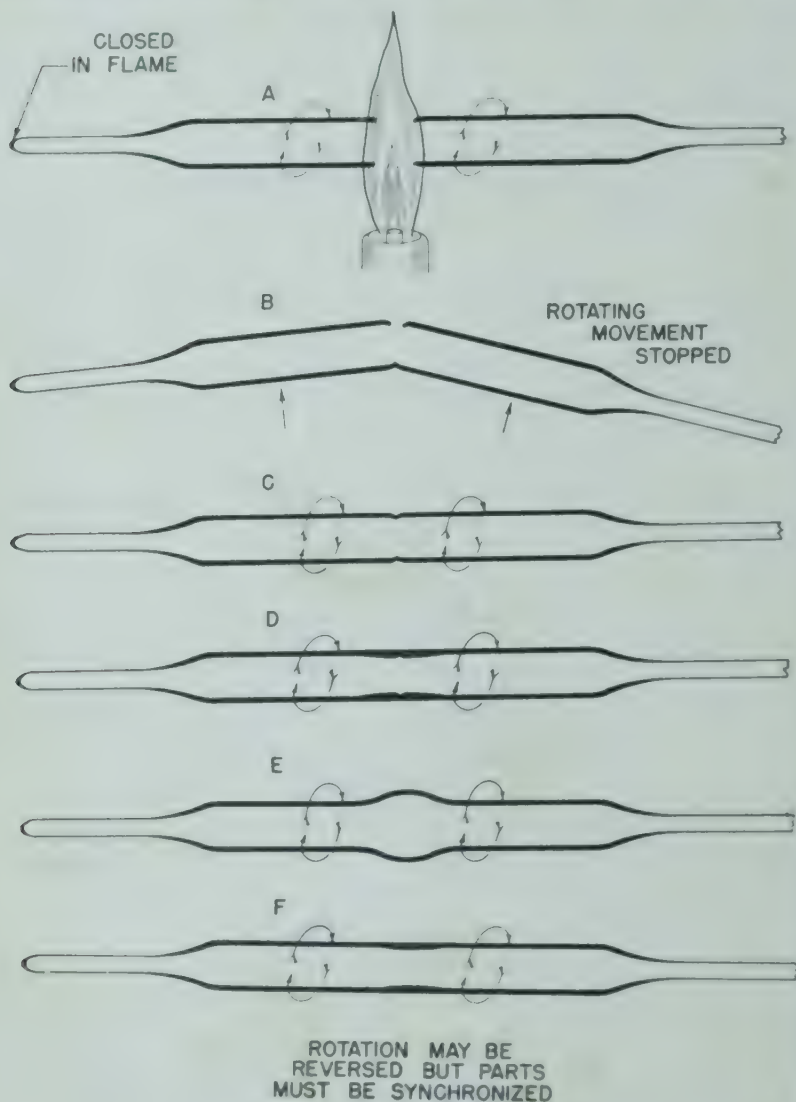


Fig. 28

held in the right hand. In removing the glass from the flame for blowing, the temporary shape of the joint must not be altered by pushing, pulling or twisting. The shape of the tubing at the seal is shown in Fig. 28E.

6. The seal, which has been blown to a diameter slightly beyond that of the original tubes, is then heated in the

flame until the glass fuses without collapsing. The enlarged portion is then removed from the flame and drawn to the diameter of the two tubes.

The principal aim in making seals is to work the glass so uniform in thickness with the walls of the tube on either side as to render the joint almost invisible. If the seal, when completed, has thinner walls than the rest of the

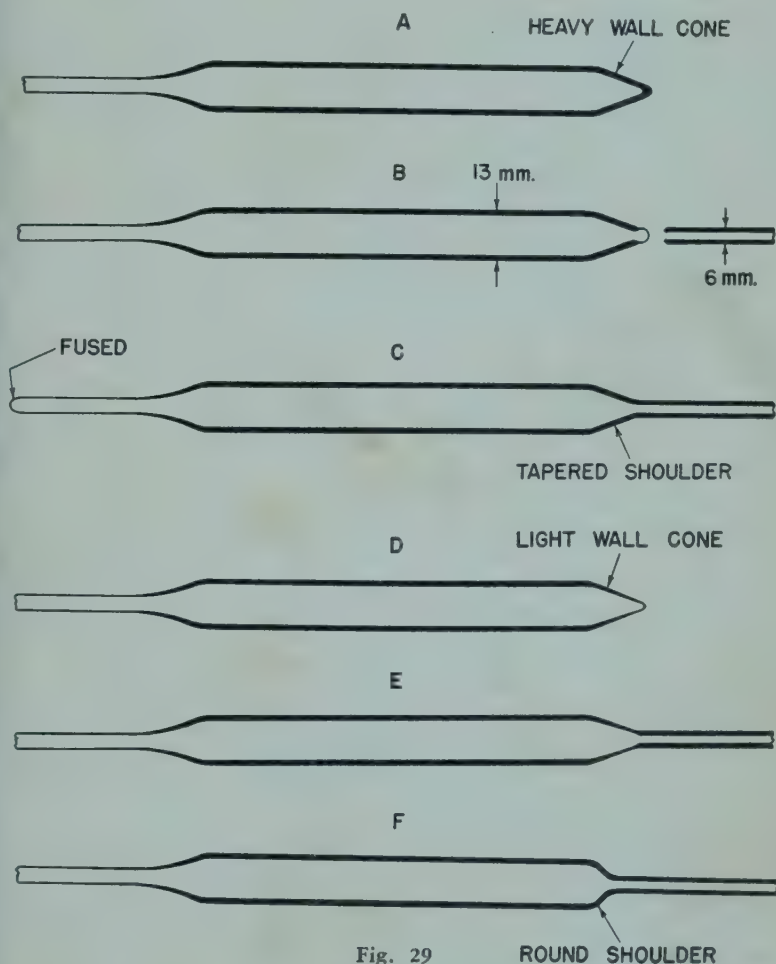


Fig. 29

tubing, it will be more easily broken.

Since glass work is largely a matter of joining glass sections, the glass worker should strive to master butt sealing completely by continued practice. Two important requirements in working glass must always be remembered in making butt seals. First, the glass tube section at the seal should be worked by collapsing and expanding the glass until a good seal is obtained. The fused glass is then

expanded slightly greater than the tube diameter. Secondly, this expanded section is drawn down to the diameter of the glass tubing.

The natural sequence toward more complicated work in butt sealing is to join together two tubes of different diameters. A suitable selection would be to join a 6-mm. tube to a 13-mm. tube. A point will not be required on the small-diameter tube, but one should be drawn on the large size. With this combination of ends, the rotation of the glass by each hand is more nearly matched. The small tube is opened by cutting with the blast burner as previously described. The larger tube is cut in a like manner but the end should be prepared so it will match the opening of the smaller tube. This is accomplished as follows:

1. The larger tube is held by the point with the left hand. The end is fused by uniform rotation and then drawn to a heavy-walled cone by attaching a glass rod to the fused glass. One should draw this cone slowly while it is

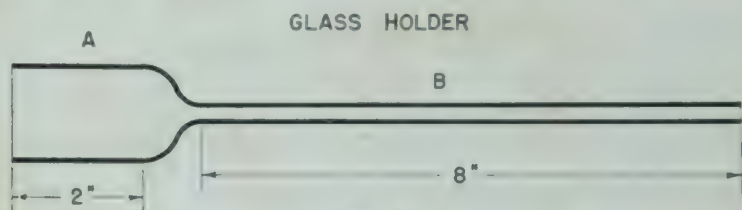


Fig. 30

rotated in the flame. After a satisfactory cone has been formed, the glass rod is removed by first allowing the cone to cool and then cutting the glass rod and excess glass beyond the apex of the cone. The finished tube is shown in Fig. 29A.

2. The apex of the cone is heated and fused in the flame until the diameter of the lens-shaped glass is that of the 6-mm. tube. The fused glass is then blown to a small bulb by quickly removing the glass from the flame and blowing into the open point end. The shape of the tube end is shown in Fig. 29B.

3. The small bulb is heated and, when the glass is fused sufficiently, it is blown out into a large thin-walled sphere. In heating the small bulb the glass of the remaining cone wall should not be fused because of the danger of enlarging the diameter of the opening at the cone apex. The thin glass is then scraped away and the opening is fire polished.

4. The two glass tubes are then sealed together as has been described under butt sealing. The small tube is left open for blowing and the point end is sealed. Care must be taken that the thickness of the glass is evenly tapered from the small tube to the large tube and that the two are

coaxial. The finished seal is shown in Fig. 29C.

This type of seal may be improved in appearance as shown in Fig. 29F. The procedure in fabricating this seal is slightly different from the cone-shaped seal.

1. The large tubing is drawn down to a thin-walled cone by fusing the glass and drawing down with an attached glass rod. The excess glass is cut away with the burner flame.

2. The cone apex is heated until the lens-shaped glass at the apex has the same diameter as the smaller tube. This glass is blown out to a small bulb and, after further heating, is blown into a sphere of thin glass. The glass of this

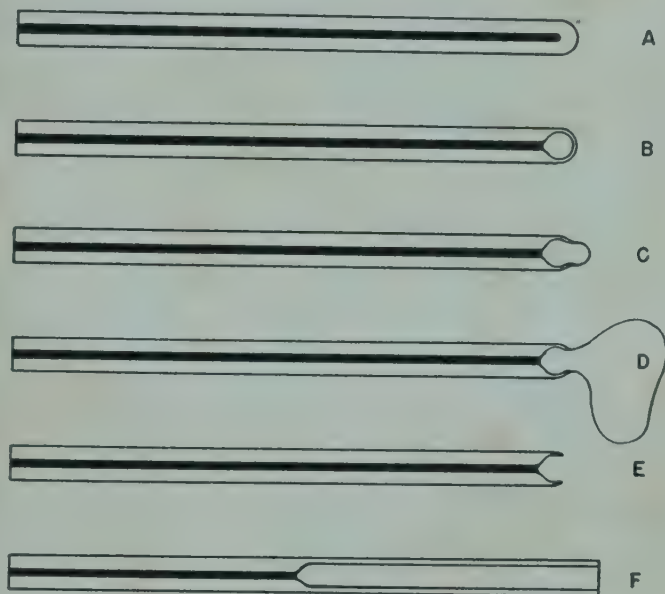


Fig. 31

sphere is scraped away and the tube end is fire-polished to a smooth square end.

3. The two tubes are sealed together as before by attaching the two fused ends and rotating in the flame as has been described under simple butt sealing.

4. The conical section is heated uniformly and blown out slowly into a hemispherical shape. The two tubes are pressed together slightly during the final blowing stage.

This technique in making reduced seals is used in preparing glass holders. The tubes are sealed as described and the large tube is cut squarely with a cutting wheel. Such a holder is shown in Fig. 30. The small tube should be about 8 mm. to 10 mm. in diameter while the larger tube should

vary in size from 18 mm. to 64 mm. These holders will serve in place of points. With a glass holder of an appropriate size, various diameter tubes can be worked by the simple expedient of wrapping asbestos tape around the glass tube and inserting it into, or around, the holder. The holder, when properly fabricated, must not wobble as it is rotated and, by proper alignment, the inserted tube will be truly axial.

The asbestos tape should be heated in a gas and air flame to burn out the binder because the smoke from hot new tape will tend to spoil seals and darken glass surfaces. Two sizes should be kept on hand: the 1" and $\frac{1}{2}$ " wide tape. It should also be quite thin (0.015") so that it can be wrapped tightly around the glass.

CAPILLARY SEALS

There is an increased demand for instruments made of glass for measurement and control purposes, such as McLeod vacuum gages, manostats, thermoregulators and rate-of-flow indicators. These instruments are generally built with a combination of bulbs, tubes and capillaries. Since the purpose of the capillary is to decrease volume or restrict flow, it must be drawn with an abnormally heavy wall for strength. In working this heavy-wall and fine-bore tubing a slightly different technique must be used.

The first exercise in handling capillary tubing is the seal of capillary to glass tubing of the same outside diameter. The steps of the procedure are as follows:

1. The capillary tube is held in the left hand and the end is fused until the bore is closed, as shown in Fig. 31A.
2. The fused end is blown out until the diameter of the bulb is equal to that of the capillary tube as shown in Fig. 31B.
3. The bulb is allowed to cool and then it is heated with tube rotation until the glass is fused at the end. The glass is then blown out as shown in Fig. 31C.
4. The extended bulb is heated at the tip until a small lens-shaped globule of glass is formed. This is quickly blown out to a thin-walled bulb, Fig. 31D.
5. The excess glass is scraped away with a forceps and the end of the tube is fire-polished in the burner flame. The final shape of the capillary tube end is shown in Fig. 31E.
6. The end of the glass tube is prepared and the seal is completed as has been previously described; care should be exercised that the capillary tube is not heated too close to the bore.

If capillary tubing is to be sealed to bulbs or tubing with diameters greater than the capillary, the same technique is used in preparing the latter. The opening on the large tube

is fabricated so the diameter of the opening corresponds to that of the capillary as shown in Fig. 31E. The heavier tube is then taken in the left hand and the seal is completed by heating the shoulder of the larger tube and working the glass by collapsing and expanding until a uniform wall thickness of the shoulder is obtained.

CAPILLARY-CAPILLARY TUBE SEALS

When two pieces of capillary are sealed together, it is preferable not to fabricate the ends as described in sealing capillary to glass tubing. Since the wall thickness requires a very hot, small and narrow flame, it is best to use a Hoke Jewel torch. The hottest point is at the tip of the noticeable

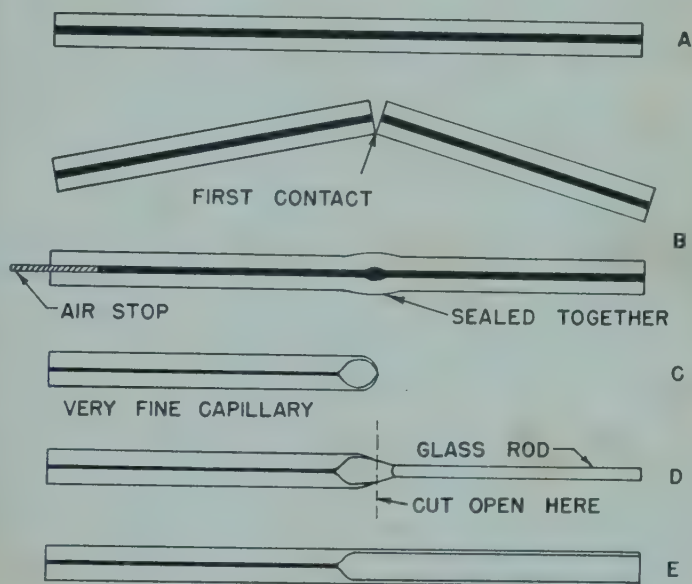


Fig. 32

bright blue flame. The procedure in completing such a seal is given in the following steps:

1. The end of one capillary is closed with a wooden air stop, while the other tube is left open for blowing. These two tubes are heated in the flame until the glass just begins to flow. They are then joined by touching the edges together on one side as shown in Fig. 32A, and brought together so the bores are perfectly aligned.

2. The seal is worked by collapsing with heat as small an area as possible, to about half the actual bore size, and expanding it with pressure to about twice the bore size. A repetition of this procedure will complete the seal as shown in Fig. 32B. Capillary seals should be carefully annealed because of their heavy walls.

Capillary-to-capillary seals are generally used in the assembly of gas-analysis equipment. A butt seal with an even- and constant-diameter bore presents a minimum of gas space which is advantageous in such systems. Generally, these systems are designed to use a standard 2-mm. bore.

It is difficult to blow through fine-bore capillary tubing. This obstacle may be overcome by the use of a reduction valve on a compressed-air line. The pressure is set at 4 lbs./in.² and introduced into the capillary through a rubber tube and metal swivel joint. The procedure in sealing this small capillary-bore tubing to glass tubing is as follows:

1. The rubber tube from the air pressure line is connected to one end of the capillary. The other end is fused by rotating in the flame. After the glass end is closed by fusion, the air pressure is admitted, regulated and shut off after a bulb equivalent to the tubing diameter is blown. The form of the bulb is shown in Fig. 32C.

2. The bulb is heated and as it begins to collapse, a glass rod is attached and the bulb is drawn out as shown in Fig. 32D and cut with a file at the point designated by the dotted line.

3. The seal is then completed by heating, collapsing and expanding the glass, the latter being accomplished by blowing through the open end of the larger tube.

ANGULAR JOINTS OR SIDE SEALS

For satisfactory results in making angular joints or side seals, a precise procedure is necessary if the seals are to have a professional appearance. A method frequently used in making a side seal is to join a tube to a perpendicular tube by butting the open end of the first to a hole on the side of other. This seal is made as the operator fuses and expands small segments of the circular seal, step by step. This method is unsatisfactory because it takes considerable time. The time element is a critical factor when side arms are being sealed on a complicated section involving closed systems and multiple ring seals. The same temperature must be maintained over-all on intricate sections. Time lost on the slow placement of side arms, with consequent spotty heating, would be costly because of the danger of undue strains in the glass. Therefore, side arms should be placed quickly with a circular movement of about a 200 to 360° swing in a plane perpendicular to the side arm. This is a skilled operation, for the art of swinging the glass through an arc of 360° in making side seals requires a good deal of practice. In addition to rotating the tubes, the glass must be fused and worked correctly to yield a seal with uniform

wall thickness. To emphasize the correct procedure in working the glass at the seal the following exercise is recommended:

1. The end of a 6" section of glass rod is fused and at-

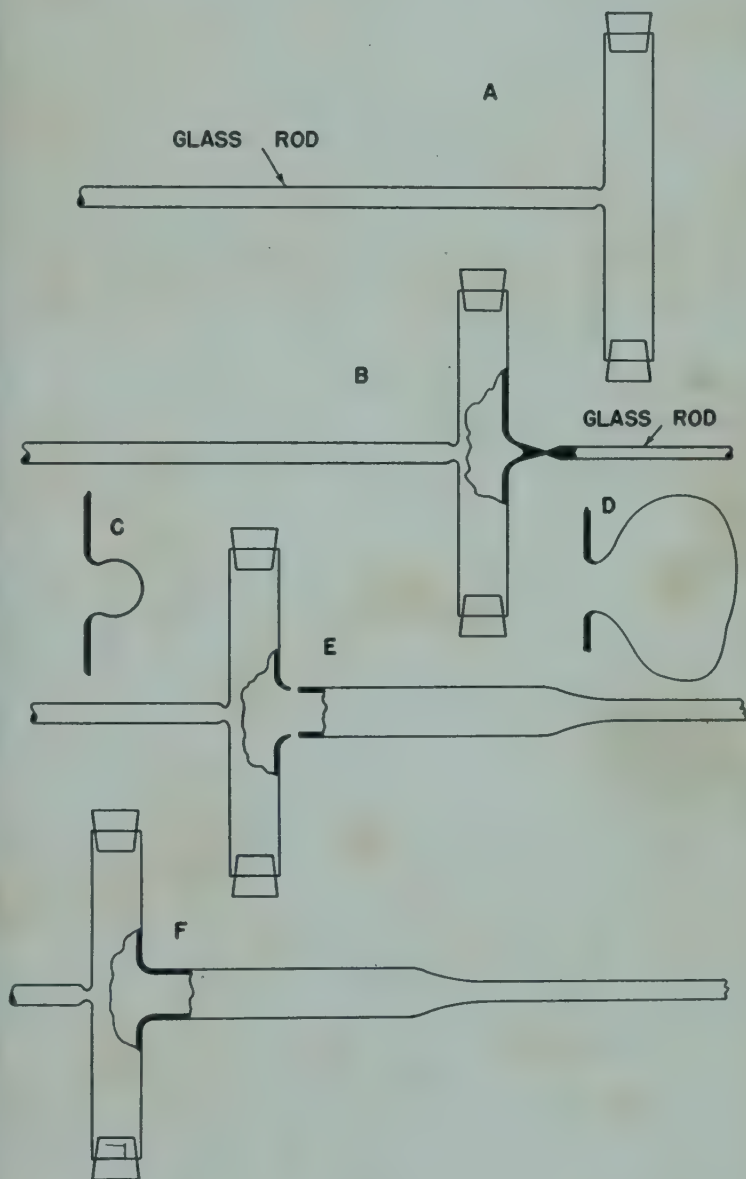


Fig. 33

tached to a glass tube about five inches long as shown in Fig. 33A. One end of the tube is closed with a cork.

2. The tube is heated exactly opposite the attached rod.

The fused glass is drawn out with another glass rod, Fig. 33B, which is held in the right hand. This rod is cut in the burner flame at the point of original contact.

3. The glass which was pulled out is fused and blown out to a small bulb as shown in Fig. 33C.

4. The small bulb is reheated and blown out to a large sphere, Fig. 33D. The glass of the sphere is scraped away and the edges are fire-polished.

5. An open tube with a point is attached to the fabricated tube by the procedure of butt sealing. The joined sections are shown in Fig. 33E.

6. The other end of the vertical tube is closed with a cork. The seal is completed by fusing the glass around the entire circumference of juncture of the two tubes with a pin-point flame. The fused collapsed glass is expanded by blowing through the open point end. The finished seal is shown in Fig. 33F.

7. The rod is cut away from the vertical tube with the flame and the small irregularity caused by removing the rod is worked until smooth.

The above procedure in making side seals cannot be used when such seals are necessary on large or complicated glass sections.

The next technique to be learned is the rotation of the glass by holding the tube. This procedure is the recommended method of making side seals and will require practice in holding the joined tubes in the flame while rotating the glass in an arc of about 200° . The procedure is as follows:

1. An opening is blown in the wall of an 8" length of glass tubing as described under steps 2, 3 and 4 of the preceding exercise. The opening in the tube should match the diameter of the tube which is to be sealed to the former.

2. The side tube is held in the right hand while the other is held in the left. The sealing edges are fused sufficiently and joined carefully to be certain that no pin-holes are left at the seal. The assembly is held in the flame as shown in Fig. 34A. The tube in the left hand is turned through an arc of 200° as the flame impinges at all times at the point of the joined tubes to insure even heating.

One should be careful not to heat the tube held in the left hand but rather to fuse the one held in the right hand sufficiently so that glass for the seal can be obtained by pushing the side tube slightly toward the joined section. This glass can then be expanded by air pressure and drawn to a uniform wall thickness.

It should be pointed out that whenever seals are made which require additional glass from one of the sections to

be joined, it is always best to work the glass slowly toward the point of the seal. The glass can then be worked sufficiently to insure a good joint and be drawn to a uniform wall thickness.

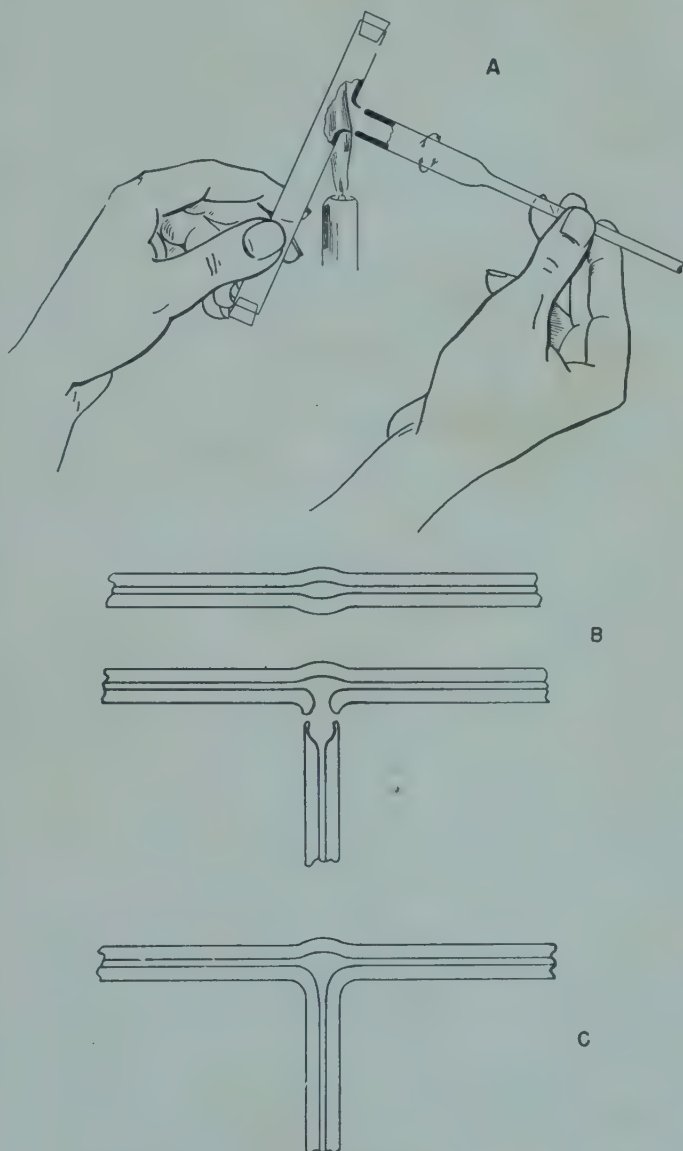


Fig. 34

CAPILLARY SIDE SEALS

The technique of making side seals or capillary tees is slightly different from that described under tubing side

seals. The sequence of steps is as follows:

1. A $\frac{1}{2}$ " section of the capillary tube is heated with rotation in the burner flame and blown out, Fig. 34B. The wall thickness of the bulb should be nearly that of the original capillary and with an internal diameter slightly greater than the capillary bore.

2. A spot on the center of the bulb is heated with a pin-point flame until the glass is fused. A glass rod is attached to the fused glass which is then drawn out to a cone-shaped form. The rod is cut away at the point of the cone. This cone of glass is heated and blown out to a small bulb which is reheated and blown out to a large thin-

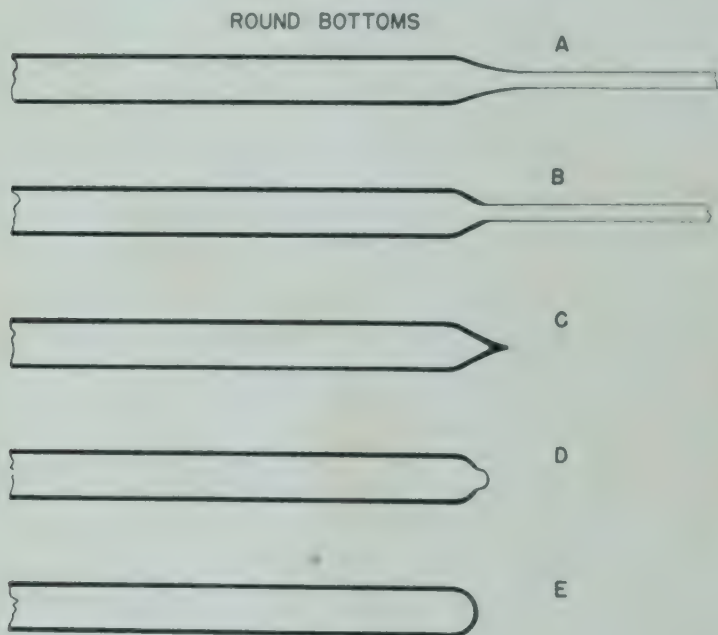


Fig. 35

walled bulb. The excess glass is scraped away with forceps and the opening is fire-polished. The opened tube is shown in Fig. 34B.

3. The procedure of opening a capillary tube has been discussed and shown in Fig. 31. A tube is fabricated as described in that section.

4. The capillary tube is sealed to the capillary with the side opening by using a pin-point flame. Only the glass at the seal should be fused. When large flames are employed, there is some danger of deforming the capillary tubing. The seal is completed by working the glass to uniform bore diameter.

ROUND BOTTOM CLOSURES AND BULBS

The glass blower frequently finds that in the fabrication of glass equipment, round bottom closures are required. The technique of making such closures is relatively simple:

1. A point is drawn on the tube by the technique described under point pulling, Fig. 35A.

2. The tube is heated at the shoulder and drawn slightly with the point to the shape shown in Fig. 35B. The glass should not be drawn too much, because the wall thickness of the cone should be identical with that of the tube.

3. The glass is cut with the flame at the cone apex by heating this zone until it is fused, and drawing away the point to form a tip as shown in Fig. 35C.

4. The tip is fused until the glass flows back toward the base of the cone. This fused glass is then blown out into a small bulb having a wall thickness comparable to that of the cone, Fig. 35D. This step is important because if the

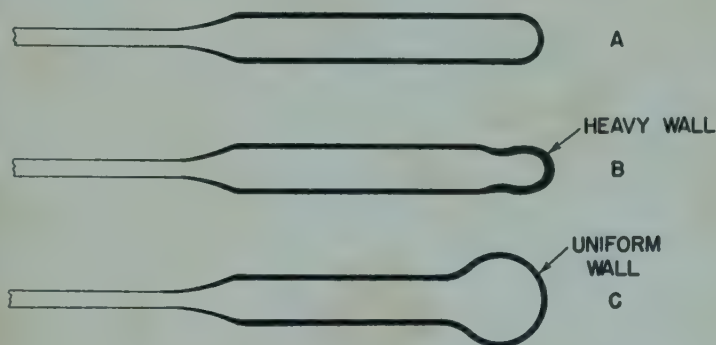


Fig. 36

wall thickness in parts of this bulb varies, it is hard to obtain a smooth rounded end. If imperfections in wall thickness are noticeable, it is best to fuse the bulb again and blow it out as described. The worker will find that timing in blowing the small bulb is necessary.

5. The cone and bulb are then heated in a medium flame under uniform and continued rotation until the glass is partly fused. The glass is blown out by holding the tube upward. The glass must never be blown out greater than the diameter of the glass tube. Any irregularities in the contour of the tube end are caused by uneven heating. The finished tube is shown in Fig. 35E.

When tubes of large diameter are closed as described above, sufficient heat must be concentrated at the end of the tube prior to the final blowing. A 4"x4"x6" wooden block fitted with a handle for holding is ideal for deflecting the hot gases of the cross-fire flames against the glass. The

block is held about an inch from the closed end of the tube.

BULB AT THE END OF A TUBE

The process of fabricating a bulb at the end of a tube is an extension of the method used in making round-bottomed closures.

1. The tube is closed as described under the procedure of making round tube closures, Fig. 36A.

2. If a bulb of normal wall thickness is desired, sufficient glass must be fused along the tube to give a section of thick-walled glass. The tube end is rotated in the flame by

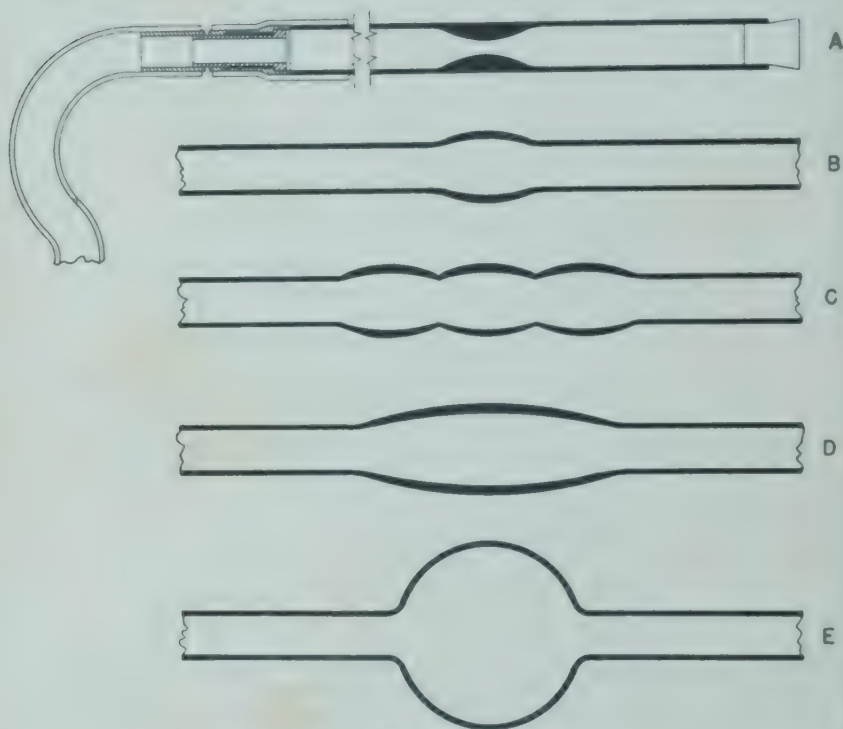


Fig. 37

holding the point in the left hand and at an angle so that gravity and surface tension both tend to cause the fused glass to flow back toward the point. The fused tube end must not be allowed to sag. The tendency to deform in this manner is minimized by holding the tube at an angle nearly perpendicular to the horizontal, or to hold the point end above the horizontal to make the glass flow in the desired direction. The appearance of the fused section is shown in Fig. 36B.

3. When the tube is taken from the flame it must be held so that the bulb formed is truly round. This is accomplished by holding the tube end up while it is slowly

expanded by blowing into the open end. The tube should be continually rotated. If a thick-walled bulb is desired it is also necessary to hold the bulb down, encouraging the flow of glass away from the tube.

BULBS IN THE MIDDLE OF A TUBE

The production of bulbs in the center of a tube section requires considerable dexterity in rotating the tube while the glass for the bulb is being accumulated. The rotation of the tube by both hands must be uniform, with no twisting of the fused glass. It is advisable to use a blowing tube with a swivel to avoid deforming the fused tube. The blowing tube is connected to the end of the tube held in the left hand while the other end of the tube is closed with a stopper. The amount of glass required for the bulb will depend on its desired size and wall thickness. This glass is accumulated as described in the following exercise:

1. The tube is rotated in the burner flame until a section is collapsed as shown in Fig. 37A. One should guard against pulling or pushing the glass during this operation.

2. The fused section is removed from the flame and blown out as shown in Fig. 37B.

3. The tube is then fused as described under (1) at a section adjacent to the blown bulb. This fused glass is blown out to a bulb comparable in diameter to the first. This procedure is repeated the third time until the final form is as shown in Fig. 37C.

4. The worked portion of the tube is then fused in a large bushy flame until the fused glass has a uniform wall thickness, Fig. 37D.

5. The glass is then blown out to a sphere as shown in Fig. 37E.

There is a definite limitation to the size of the bulb that may be blown as described because of the dexterity required in handling large sections of fused glass. The walls of bulbs blown in this manner usually are thin and no additional outlets can be sealed to the bulb.

Thick-walled bulbs are more easily fabricated by using a tube with a diameter equal to that of the bulb.

1. As an example, suppose a bulb of 2" diameter is required with two opposite tube connections of 8-mm. diameters. A short section of 51-mm. tubing can be used by placing it on a fabricated holder. Asbestos tape is used as a packing medium. The open end of the tube is closed as described under round-bottomed closures. The fabricated tube is shown in Fig. 38A.

2. The tip of the round bottom is heated by rotating the tube until a small portion of glass is fused. This glass

is drawn out to a cone with a glass rod, Fig. 38B. The cone is opened by fusing and blowing to a small bulb equivalent in diameter to the 8-mm. tube. The tip of this bulb is heated until the glass is fused back to the maximum diameter of the small bulb and then blown out to a large thin-walled sphere. The glass of this sphere is brushed away with forceps and the opening is fire-polished. The 8-mm. tubing is then sealed to the rounded bulb, Fig. 38C, by the procedure of butt sealing, Fig. 38D.

3. The 8-mm. tube is held in the left hand and the large tube is heated just beyond the point, which is to be the maximum diameter of the bulb. The tube is drawn down, Fig.

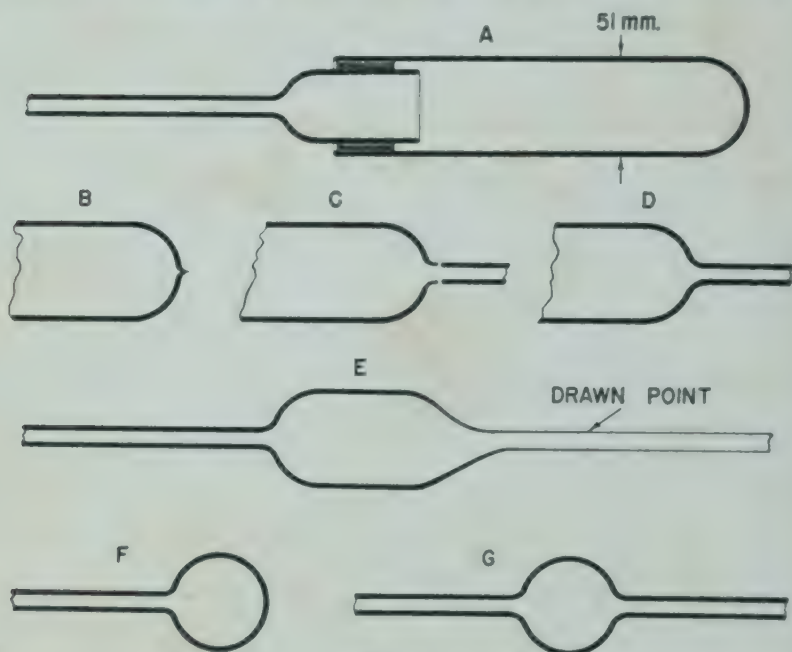


Fig. 38

38E, and the end is closed as described under the fabrication of rounded tube closures, Fig. 38F.

4. The tip of the bulb is then fused and the same procedure as given under (2) is followed in sealing the second tube to the bulb, Fig. 38G.

It is advisable to incorporate all standard flask sizes, which are already fabricated in perfect spheres, for bulbs in gas-sampling containers, reservoirs or other equipment requiring bulbs of various sizes.

OPEN AND FLARED TUBE ENDS

Apparatus or instruments of glass should be built with critical attention to details which enhance the appearance of the completed work. One of the simplest operations, and

yet the most neglected, is the form of open tube ends.

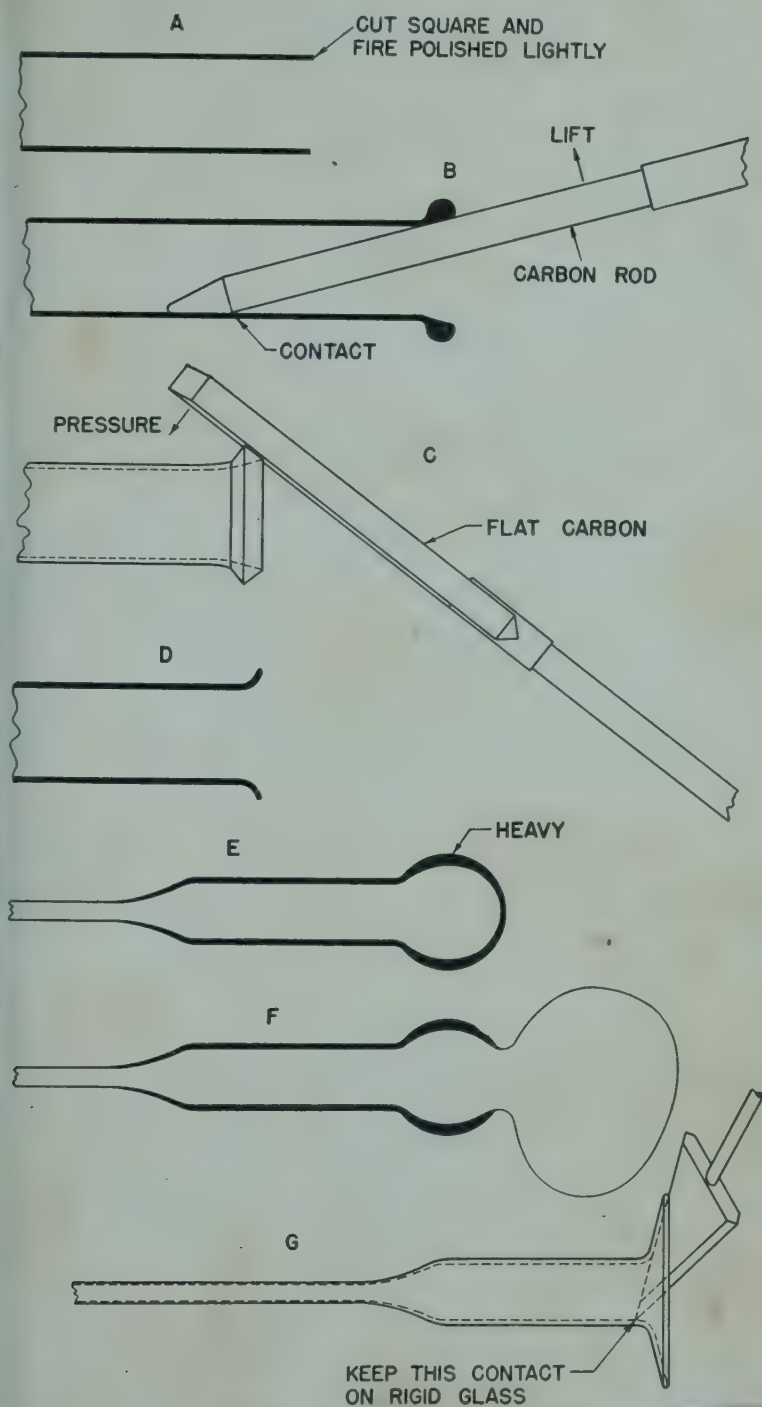


Fig. 39

OPEN ENDS

Square-cut Ends.—If it is required, in auxiliary equipment, that the end should be square, the tube is cut with an abrasive wheel or hot wire cutter and fire-polished until the edges are smooth, Fig. 39A.

Reinforced and Tapered Ends.—Sometimes it is necessary to reinforce the end for stoppers. This may be accomplished as shown in Figs. 39B and 39C. The tube end is fused by supporting the glass on rollers and heating the glass sufficiently so that surface tension causes the glass to accumulate at the end. This glass is then worked with a round carbon tool, Fig. 39B. The point of contact of the end of the tool is on the cooler side of the glass which makes it possible to apply a little force in forming the fused portion.

Beaded Ends.—Another method for preparing a tube end is shown in Fig. 39C. The end of the tube is prepared as shown under Fig. 39B. The glass is allowed to cool until rigid. The very tip of the end is then heated in a hot flame and shaped as shown in the drawing. The entire bead should not be fused in this operation because of the danger of greatly restricting the opening. Even under the most carefully controlled conditions it is necessary to heat the end sufficiently to permit opening of the end with a standard taper. The tube, however, should not be so heated that the square end will be deformed. Heavy ends should be carefully annealed after they are completed.

Curved Ends.—A tube end with a curved edge comparable to test-tube ends is fabricated by fusing the very end of the glass just to the point where it can be worked to a flared end, Fig. 39D. The glass must not be allowed to thicken as was required in preparing the tooled ends discussed above.

FLARED ENDS

Flares on tubing ends have other uses as well as serving as a finished end. The limitations of the width of the flare are determined by the diameter of the tubing. In making large flares on small tubing the expedient of expanding the end of the tube to a thick-walled bulb is used, rather than attempting to spin out the small diameter tubing to a large heavy-walled flare. The recommended method of flare fabrication is as follows:

1. A strong and truly axial point is drawn on the tube. This is important since the non-axial points will cause poor and irregular flares. The tube is held by the point in the left hand and the outer edge of the end is softened by partial fusion. The flat-pointed tube is applied horizontally

into the end of the tube, by the right hand, with a gentle pressure against the side of the tube as it is rotated in a clockwise and counter-clockwise movement. The tool is gradually swung upward toward the left hand so that the flare is gradually worked to the desired form, Fig. 39G. The flare is formed, not by heating it entirely as it is made, but rather by working it from outer flare edge to the tube by heating circular portions of the flare. Pressure on the tool is carefully controlled in shaping the glass which must

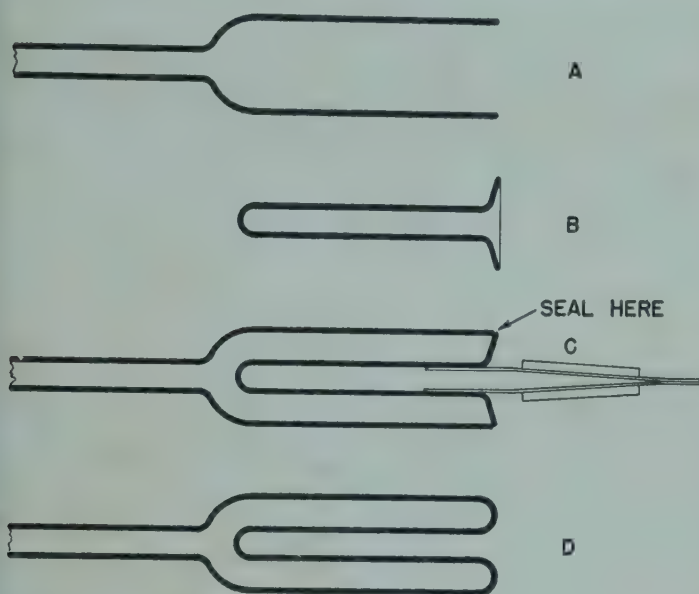


Fig. 40

be soft enough to be gently shaped at the slightest contact of the tool. Increasing the pressure will deform the glass.

On some occasions it is necessary to make wide flares on tube ends. This can best be accomplished as follows:

1. A truly axial point is drawn on the tube which is in turn closed and blown into a thick-walled bulb, Fig. 39E.

2. The bulb is cut open by fusing the glass from the tip to the maximum diameter of the bulb. This fused glass is blown out to a thin-walled bulb, Fig. 39F. The thin glass is scraped off and the edge is fire-polished.

3. The flare is then completed as described above and shown in Fig. 39G.

FLARE SEALING

The flared end is used in an application where one tube is to be sealed within another tube of larger diameter. This seal is made by the following procedure:

1. A point is drawn on one end of the larger tube. The

other end is opened to a square end with the burner flame, Fig. 40A, as was previously described.

2. A flare with a diameter equivalent to that of the large tube is made on the smaller one. The end opposite the flare is closed to a round bottom, Fig. 40B.

3. The flared tube is placed inside the larger tube by supporting the former with forceps, Fig. 40C. The two edges are fused together and the forceps is removed. The seal is worked by heating with uniform rotation and blowing out the collapsed glass. *Important:* When the glass at the seal is soft, the inner tube will have a tendency to sag and must therefore be balanced by clockwise and counter-clockwise motion. Should the inner tube become constricted, it can be opened only by applied pressure with a round carbon rod held against the top of this tube. Enlargements on the outer tube can be worked to the tube diameter with a flat carbon tool. When completed, both tubes should be symmetrical, Fig. 40D. The seal is carefully annealed.

CHAPTER III.

THE FABRICATION OF MULTIPLE GLASS SEALS

Condensers, liquid traps, vacuum-jacketed distillation columns, diffusion pumps, liquid-level controllers, as well as numerous other parts of special glass equipment, require in their fabrication the use of the internal, triple or commonly-called ring seal. This seal is located where one tube passes through the end or side wall of another and actually forms a ring at the juncture of the tubes. The methods of making this seal may be divided into two classes:

1. The inner tube is not supported when the seal is made.
2. A support of the inner tube is necessary because of its weight or position.

RING SEALS WITH INNER TUBES UNSUPPORTED

The simplest ring seal is the type in which a short length of tubing is sealed into a larger tube. The beginner must master this seal on a small scale to be successful in more complicated work where more than one or larger ring seals are required. The steps in making a ring seal with an unsupported inner tube are illustrated in Fig. 41.

1. A tube with a diameter of approximately 16 mm. is drawn to a point. This point is then held in the left hand and the opposite open end is closed by fusing the glass, attaching a glass rod and pulling the tube end to a cone. In this step one must not forget that the glass tube should be rotated in the burner flame for even wall thickness in the cone. The tube is opened at the apex of the cone by heating this point until the lens-shaped form of fused glass has the diameter of the smaller tube which is to be sealed into the prepared opening. This glass is blown out to a small bulb, reheated and finally blown out to a thin-walled glass sphere. If one is careful in scraping away the glass, a small flare is retained as a foundation for the ring seal, Fig. 41A. The opening should be about 11 mm. in diameter.

2. A small tube, 10 mm. in diameter, is heated at the desired location for the ring seal. A short section, $\frac{1}{2}$ " in length, is fused and a small bulb is blown. Immediately after the bulb is blown and while the glass is still in a plastic state, the two ends are pushed together to form a tube section as shown in Fig. 41B. The outside diameter

of this glass shoulder should be only slightly larger than the diameter of the opening on the larger tube.

3. The open point end on the large tube is sealed and the smaller tube is placed in position so that its shoulder rests on the small flare at the opening of the large tube, **Fig. 41C**.

4. The ring seal is made by holding the two tubes together while rotating them in the flame. The glass should be fused sufficiently at the juncture of the two tubes to yield a good leakproof seal. Subsequent collapsing and expanding at the seal is required to work the glass. During this work one must be careful to balance the inner

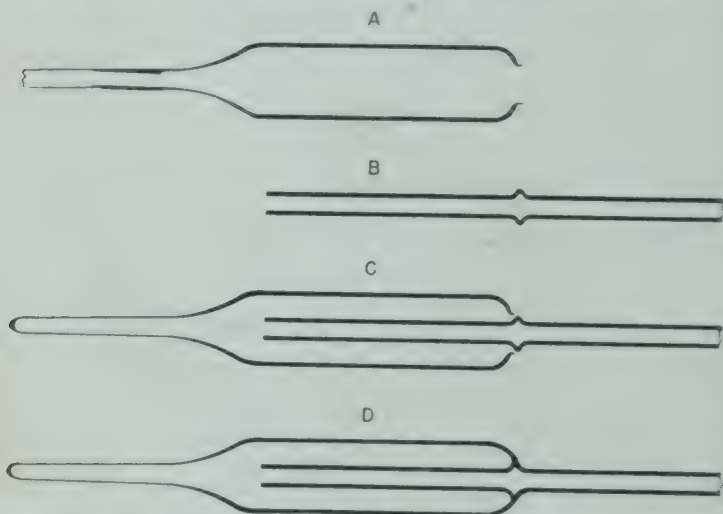


Fig. 41. (*Drawings by Richard P. Jones, Gulf Res. & Dev. Co.*)

tube by adequate rotation. After the seal has been completed it is heated sufficiently for final alignment of the center tube. It is then annealed. The completed seal is shown in **Fig. 41D**.

It is frequently desirable to butt seal a side arm on the shoulder or rounded portion of the large tube. When a side arm is required, as in the case of condensers, the ring seal must be kept hot to prevent it from cracking while the side arm is being attached. The latter, if placed near the ring seal, will be most efficient functionally if the fabricated glass is to serve as the end of a condenser. Side arms close to the ring seals are also required for traps.

The fabrication of a suitable side arm will depend upon the shape and form desired for connecting auxiliary equipment. It is also important to make the side arm before the ring seal is started so that no time is lost in butt sealing the former to the outside tube. Under such conditions the finished ring seal need not be reheated. The successive

steps in making a side arm for a rubber tube connection are given in the following steps.

1. A point is drawn on the glass tubing as shown in Fig. 42A.

2. The tube is then constricted by fusing the glass at a point one inch from the shoulder of the point. The tube must be rotated in the burner flame and one must be careful not to pull or push the ends of the glass while the constriction is being formed, Fig. 42B.

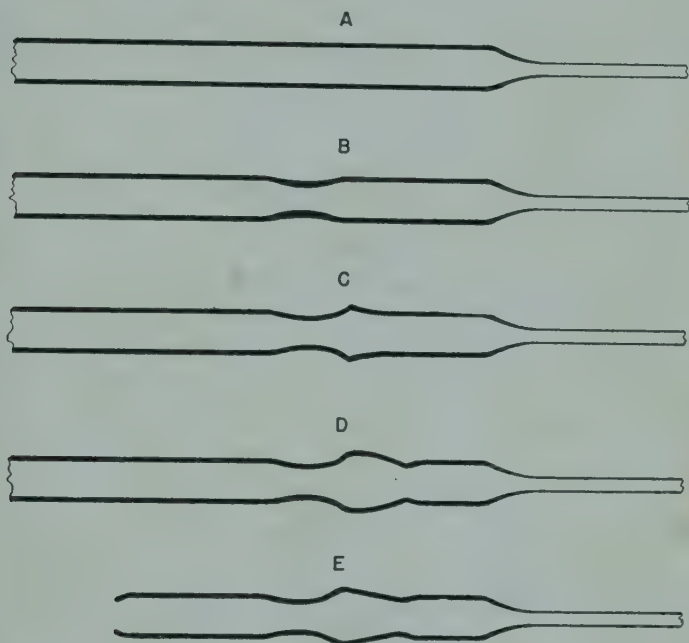


Fig. 42

3. The glass is then heated at the right of the constriction until the glass begins to soften sufficiently so the tube can be pushed together to form a small bulge, Fig. 42C.

4. The glass to the right of the bulge is constricted by fusion, Fig. 42D.

5. The tube is then cut to the desired length by technique of preparing a tube end for sealing, Fig. 42E.

6. The side arm is sealed to the glass tube containing the ring seal by the procedure outlined under butt sealing. One should be careful to keep the ring seal hot while the side arm is attached. The position is shown in Fig. 42A or B.

The fabrication of uniform and reproducible drop counters is quite important in the production of ebulliometers. The ring seal is made by using a special inner tube which is fabricated as illustrated in Fig. 43D and E.

1. The counter is formed by fusing the end of a glass rod until the fused ball has the required diameter, Fig. 43D. The diameter is increased by fusing the glass of the rod and allowing the glass to flow to the glass sphere. The rod must be rotated during the fusing process.

2. The inner tube is prepared by heating a short section and expanding the fused glass with air pressure. The tube ends are pushed together during this operation to form a small shoulder of glass.

3. The end of the dropper is completed by bending the tube to one side of the shoulder, Fig. 43E. The tube is cut at the bend with the flame and the ball is attached by fusing

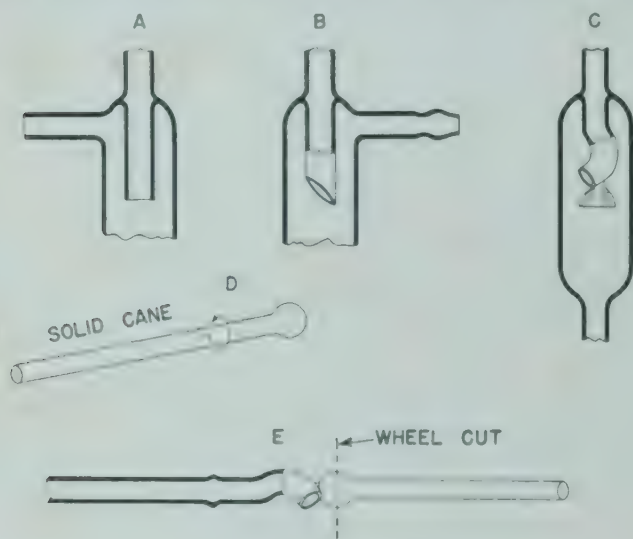


Fig. 43

both the one edge of the tube end and the ball and pushing the two together. The ball is then cut on the cutting wheel at the center indicated by the dotted line, Fig. 43E.

RING SEALS WITH INNER TUBE SUPPORTED

The inner tube of a ring seal must be supported when it is long and heavy or when the tube is to be sealed in a definite position as through the side wall of the larger tube. Ring seals are best made by applying air pressure to both sides of the inner tube. The fabrication of glass holders for supporting one tube has been described as simply butt sealing a small tube to a larger tube and cutting the latter with an abrasive wheel. When inner tube supports are required, a holder is fabricated as illustrated in Fig. 44A.

1. One end of the holder is made by butt sealing a small tube to a large tube. Instead of cutting the latter on the end opposite the seal, a second tube is butt sealed to the

large center tube. This small tube is cut with an abrasive wheel to the desired length, Fig. 44A.

2. It has been pointed out that in the fabrication of ring seals, means of applying air pressure to both sides of the inner tube are necessary. If the larger end of the holder is to be used for applying air pressure, openings on the

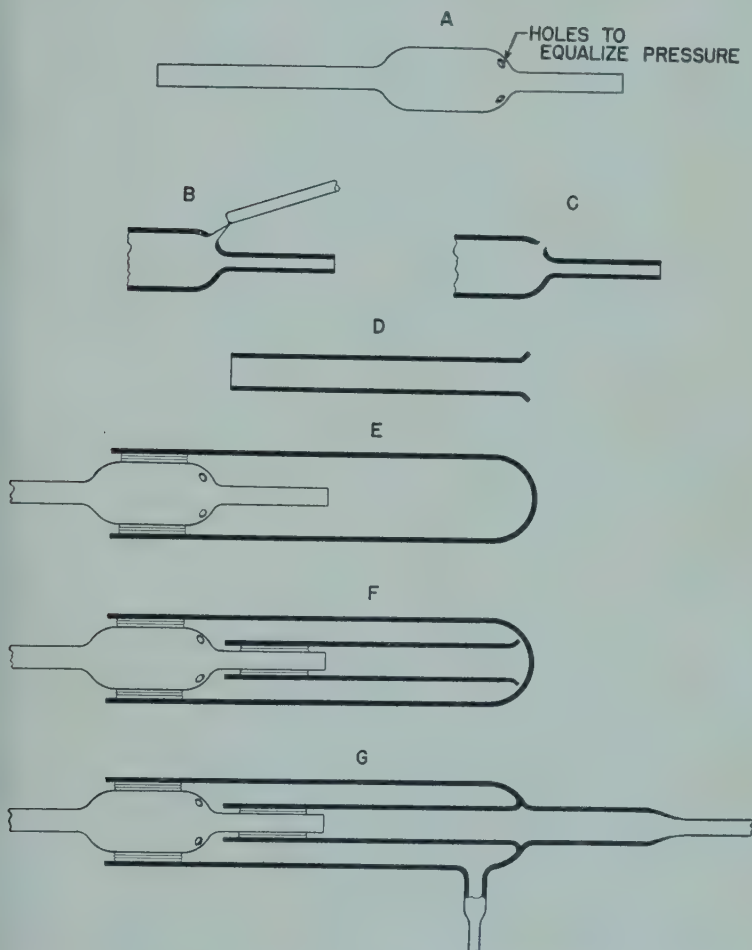


Fig. 44

shoulder near the seal of the smaller tube will make it possible to obtain pressure in the tubing assembly. These openings are made by heating a spot on the large tube shoulder until the glass is fused and then drawing out the fused glass with a glass rod, Fig. 44B.

3. The thin cone-shaped glass is scraped away and the opening is fire polished, Fig. 44C. Three or four openings are sufficient.

After the openings are made, the holder should be rotated in the left hand to test the smaller tube for exact alignment. Several holders with different tube sizes and lengths should be prepared for future use in the fabrication of ring seals.

A definite procedure should be adopted when glass equipment is being made. The beginner will find that considerable time is saved if the various parts of the proposed equipment are first prepared. This is especially important when ring seals are involved because once the equipment is being assembled the work need not be interrupted until all seals are made. The reheating of a ring seal which has been allowed to cool is time consuming.

The production of a ring seal by supporting the inner tube is best performed by first making the integral parts required for the total assembly.

1. The inner tube is flared by rotating the end of a tube in the burner flame and opening it with a triangular flaring tool. One must be careful to prepare the flare with uniform wall thickness, Fig. 44D.

2. The outer tube is made by supporting one end of an open tube length with a holder. Asbestos tape is used for holding the tube on the holder. The opposite end is closed to a round end, Fig. 44E.

3. The side arm and the tube extension of the inner tube are prepared as previously described. Both should have axial points.

4. The inner tube is supported on the small tube end of the holder by using asbestos tape. The outer tube is then supported on the enlarged section of the tube holder with asbestos tape, Fig. 44F.

5. The tip of the round end of the larger tube is fused by rotating it in the burner flame until the glass of this large tube is fused to the inner tube.

One should be careful not to collapse the glass of the outer tube behind the point of contact between the tubes. The fused glass is blown out slightly and fused again to insure a good seal between the inner and outer tubes. The glass covering the flared end of the inner tube is then fused and blown out to a small bulb. This bulb is heated with rotation until the glass is fused to within an eighth of an inch from the ring seal and blown out to a thin walled bulb. The glass is scraped away with a forceps and the end is fire polished. The inner tube extension which was prepared before the ring seal was started is immediately butt sealed to the opened ring seal. The open point end of the inner tube extension is used for applying air pressure while the open end of the dual tube holder is closed with a small cork.

After the butt seal of the inner tube is completed the side arm is immediately sealed to the outer tube, Fig. 44G. The entire assembly is then annealed and allowed to cool. The holder is then carefully removed.

A ring seal at the wall of the outer tube is frequently required and is made by using the dual glass holder. All parts of the complete assembly should be made before the ring seal is started.

1. The inner tube is made by bending a glass tube at a right angle. The tube is cut squarely with the flame and fire polished. It is important that the end be square, Fig. 45A.

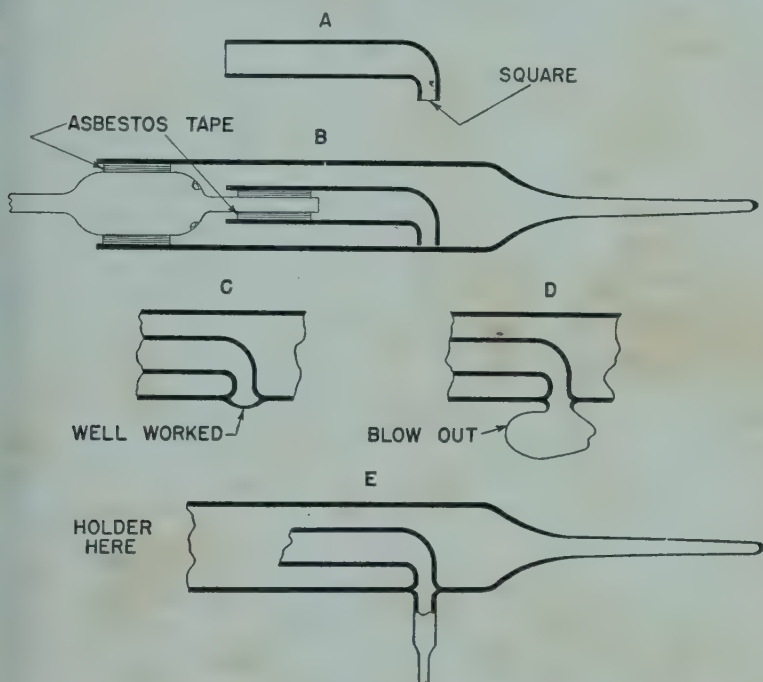


Fig. 45

2. The extension for the inner tube is prepared in the usual manner by first pulling a point on the tube and then opening the other end with the burner flame.

3. The outer tube is mounted on the glass holder with asbestos tape and a point is drawn on the tube. The holder is then removed and the inner tube is mounted on the holder tube. The inner tube should be centered and should also touch the outer tube wall. The outer tube is mounted as shown in Fig. 45B.

4. The outer tube is rotated in the burner flame until it is hot but not to the extent that it is pliable. It should be heated periodically in this manner as the seal is made. The outer tube is then heated at the point where the inner tube

touches the outer tube wall until the glass is fused sufficiently to form a seal with the inner tube. The glass at this point is worked by blowing it out, Fig. 45C, and collapsing it by fusion.

5. After a good seal is obtained at the juncture of the inner and outer tubes, the glass is fused and blown out to a small bulb which in turn is fused and blown out to a thin-walled sphere, Fig. 45C. The excess glass is scraped away and the opening is fire-polished.

6. The tube extension is sealed to the ring seal. The point of this tube is used for applying air pressure while the glass holder end is closed with a small cork. The procedure used in making this seal is simply a side arm sealing technique. The completed seal is annealed and allowed to cool. Extreme care must be taken in removing the glass holder because of the torque which can be developed if the end of the holder is moved away from the true center. It is best to remove the holder by pulling it out with slow rotation.

Whatever types of ring seals are required, or whatever method is used in making them, ring seals at the opposite ends of two annularly spaced tubes present the problem of completing the seals without setting up too many stresses at the fabricated ends. After both seals are completed the outer tube must not be heated rapidly or expansion will cause the inner tube to break because of strains.

The fabrication of a glass condenser will be considered next in the study of ring seals. All parts such as inner tube extensions and side arms are made before the work on the condenser is started.

1. The one end of the outer tube is prepared as described and shown in Fig. 41A. A glass holder is used to hold the tube instead of drawing a point, because the inner tube is inserted through the open end. The end which is opened by the burner flame should, in this case, have an opening slightly smaller in diameter than that of the shoulder of the inner tube. This tube is also flared at the end where the second ring seal is to be made. The flare is slightly smaller in diameter than the outer tube opening so that the inner tube can be inserted in the larger tube. If this tube is long or heavy, it should be supported by inserting a dual glass holder into the large tube end as well as the inner tube. The glass at the juncture is heated and the seal completed as described before and shown in Fig. 41A.

2. A second method of making the first ring seal would be to follow the procedure outlined in Fig. 44. The inner tube is flared on both ends and inserted into the outer tube which has a rounded end. The seal is made as previously described and as shown in Fig. 44E, F and G. The side arm

serves as an opening for applying air pressure to the outside of the inner tube when the second ring seal is made. The ring seal is then annealed.

3. The glass extension of the inner tube which was sealed at the ring seal is taken in the right hand after the end is cool, Fig. 46A. The holder is removed and the open end of the large tube is drawn to a point so that the shoulder formed almost touches the flare, Fig. 46B. This shoulder is

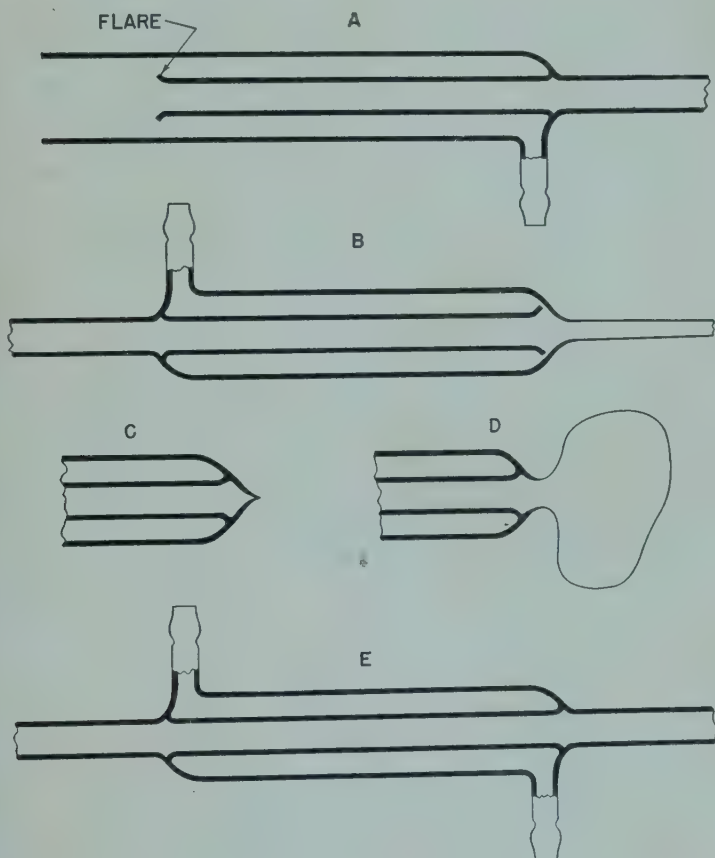


Fig. 46

heated until the glass collapses and forms a seal at the flare edge. A good seal is made by pulling away the excess glass, Fig. 46C, and working the glass at the seal by repeated collapsing and expanding. The application of air pressure to the side arm will keep the outside tube from collapsing behind the ring seal. The end is then heated and blown out to a thin-walled glass sphere which is scraped away. The end is fire-polished and the tube extension is butt sealed to the condenser. The side arm is attached close to the ring seal. The glass is then annealed.

SPECIAL CONDENSERS AND JACKETED BURETTES

There are occasions when special inner tubes or a section or sections of several bulbs are required for condensers or constant-temperature gas burettes. No elaborate inner tube holder need be used because of the size of the inner tube assembly. Several strips of tape are sufficient for holding the tube.

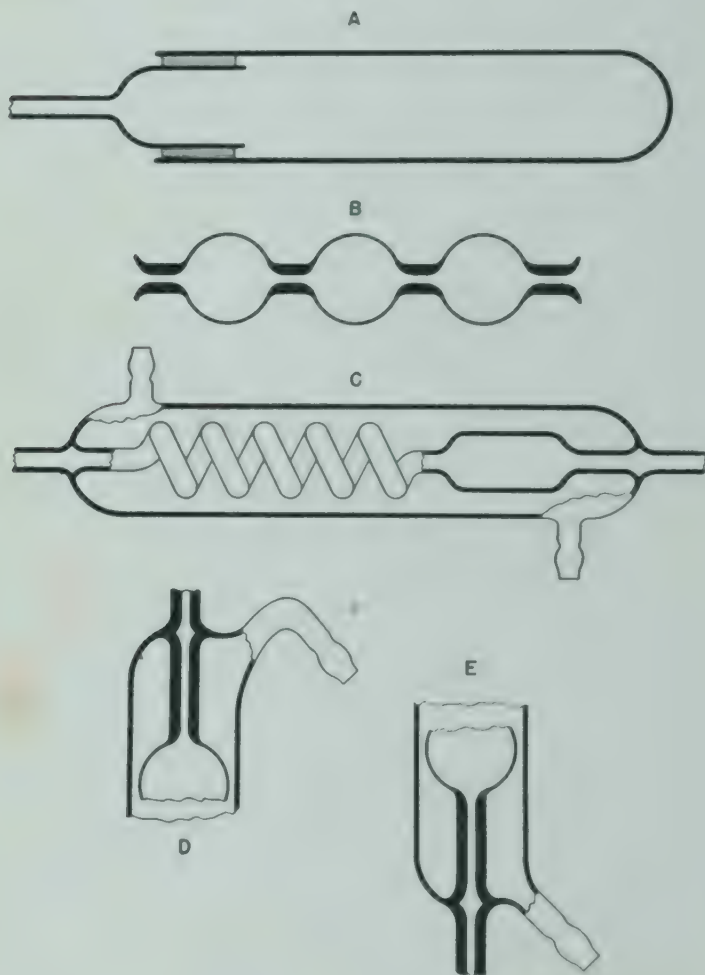


Fig. 47

1. The outer tube which is to serve as a jacket is rounded at one end as shown in Fig. 47A. The technique in making round bottoms on large tubings has been described and shown in Fig. 35.

2. The bulb assembly, Fig. 47B, is fabricated by making three bulbs by the procedure described before and shown in Fig. 38. Capillary tubing (2 mm.) is sealed to both openings of the first bulb while only one capillary is sealed to

each of the remaining bulbs. One capillary tube is used as a handle which is held in the left hand. The second capillary tube is opened by the flame at the desired point. The second bulb which has but one capillary tube sealed to one opening, with the second opening as prepared in Fig. 31, is sealed to the capillary of the first bulb. The capillary of the second bulb is cut with the burner flame and the third bulb is sealed to the assembly.

3. The fabricated bulb assembly now has a capillary tube at each end. One tube is opened near the large bulb with the burner flame by first making a small thick-walled bulb. This small bulb is cut at its largest diameter by heating and fusing the bulb at the tip until the glass is fused to the diameter of the bulb. This fused glass is blown out and removed by scraping away the thin-walled sphere. The end is fire-polished and flared with a round carbon tool. The glass is allowed to cool and the second end is prepared in a similar manner.

4. The inner tube assembly is then put into the outer tube. Several strips of asbestos tape, between the bulb nearest the open end of the outer tube, and the outer tube, will be sufficient to hold the assembly for the fabrication of the ring seal.

5. The inner tube extensions and the two side arms are prepared before the work is continued.

6. The first ring seal is made and the side arm is sealed to the outer tube. It is desirable to bend the first side arm as shown in Fig. 47D to prevent kinking of rubber tubing if the jacketed condenser or burette is used in a vertical position. The second ring seal is completed and the side arm is sealed as shown in Fig. 47E. The ring and side arm seals are annealed as soon as they are completed.

A condenser with a combination spiral and straight inner tube is shown in Fig. 47C. Fabrication of spirals will be described later. The condenser is made exactly as has been described under the procedure outlined for making the glass-jacketed gas burette.

It is not necessary to describe the various designs of condensers or traps which could be made. There are many types of commercial condensers and traps which can be obtained for specific laboratory work. One condenser which is useful will be described because several types of ring seals are required in its fabrication. This condenser consists of a combination of a straight water jacket and pencil condenser, Fig. 48D.

1. Four different tube sizes are chosen to properly proportion the annular spaces and to allow a maximum distance for the side wall ring seals. The lengths of the respective tubes will depend on the desired length of the condenser.

2. The pencil condenser is made by the procedure outlined for making a simple trap. The inner tube is supported only if it is long and heavy. A small point at the end of the condenser will aid in causing reflux to drip from the end of the pencil condenser. The extension or center tube is bent at a right angle. Both this tube and the side arm tube are cut in the burner flame and flared so that the entire

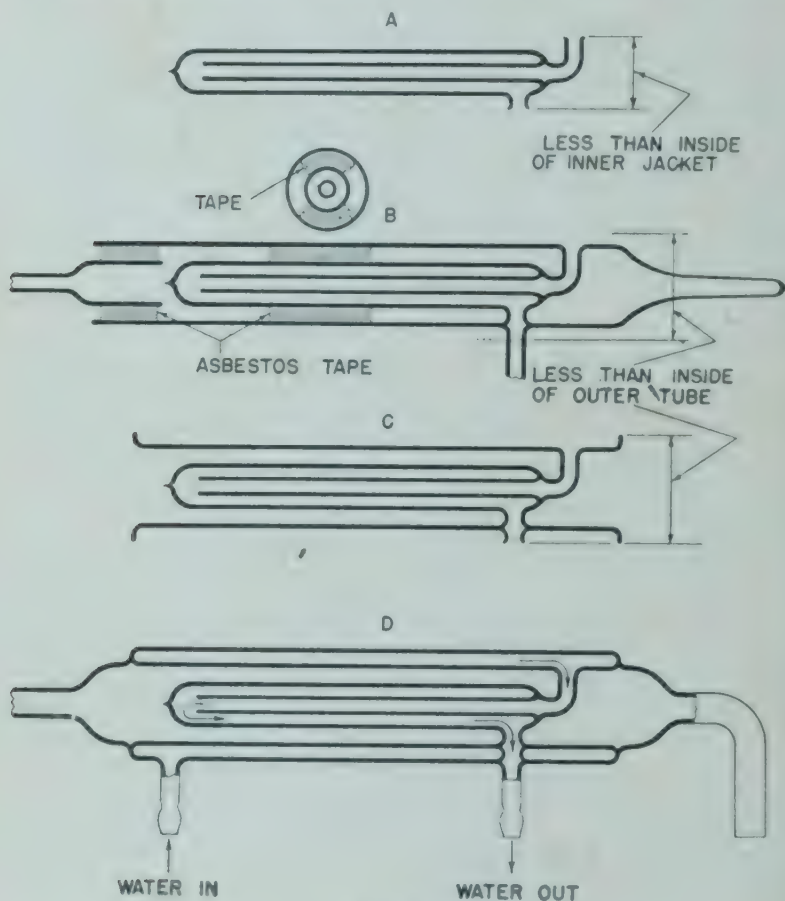


Fig. 48

diameter is a little smaller than the inner jacket tube. Fig. 48A.

3. An axial point is drawn on the inner jacket tube and the pencil condenser is put into the inner tube and held in place with tape, Fig. 48B.

4. A glass holder is taped to the end of the inner tube of the proposed outside condenser and the point end is closed by sealing the glass. Three side arm tubes are then made, two of which are fabricated for hose connections. The ring seal is made first by heating the outer tube by ro-

tating it in the burner flame and then fusing the glass of the outside tube until a seal is made with the side arm of the pencil condenser. The glass is blown out slightly by applying air pressure to the open end of the glass holder. One must be careful that the glass covering the opening is fused sufficiently to be blown out to a small bulb without deforming the glass around the outside of the point of contact. The glass covering the side arm is blown out and the straight side arm with a drawn point is sealed to the assembly. *This tube* is used for applying air pressure in blowing out the glass over the second tube. The glass holder opening is then stoppered and the seal at the opposite side is made by fusing the glass until it collapses on the tube opening. At this point it is desirable to remove a certain amount of glass covering the opening by drawing it out, after it is fused, with a small glass rod. The remaining glass is worked by repeated expanding and collapsing to insure a good seal; and the remainder is blown out and removed with a forceps. The tube on the ring seal is then cut and flared slightly at the point indicated by the dotted line, Fig. 48B. The assembly is then carefully annealed.

5. The outer tube is cut at the desired length and each end is flared, Fig. 48C. The flares should have a wall thickness comparable to that of the tube.

6. If the flares and the side tube from the ring seal are carefully made to conform to the inner jacket tube diameter, the fabricated assembly can be easily inserted into the outer jacket tube. The seal nearest the proposed side wall ring seal is completed first. The side wall ring seal is then made by sealing on the extension hose connection tube previously prepared. The entire end is carefully annealed. After the glass has cooled sufficiently for handling, the ring seal is made at the opposite end. It will be necessary to connect a blowing tube to both the side arm and the ring seal extension tube to permit blowing on both sides of the seal. The second side arm is then sealed to the jacket before the ring seal cools. Air pressure is applied through the first attached side arm. The end is then annealed, Fig. 48D.

SPECIAL RING SEALS

A condenser which is particularly useful in the fabrication of diffusion pumps is shown in Fig. 49A. The outer tube which serves as one wall of the condenser is straight; and the inner tube is flared for contact at the ring seal. The construction of this type of condenser is not difficult, except that the flares of the inner tube must be spun out to give even contact along the entire diameter of the outside tube.

1. Two side arms are prepared as illustrated in Fig. 42. One will have to be long enough so that a right-angle bend can easily be made.

2. The one end of the outside tube is drawn to a point. Sufficient tube length must be allowed for the flared inner tube and the other end of the tube is cut squarely with an abrasive wheel or hot-wire glass cutter.

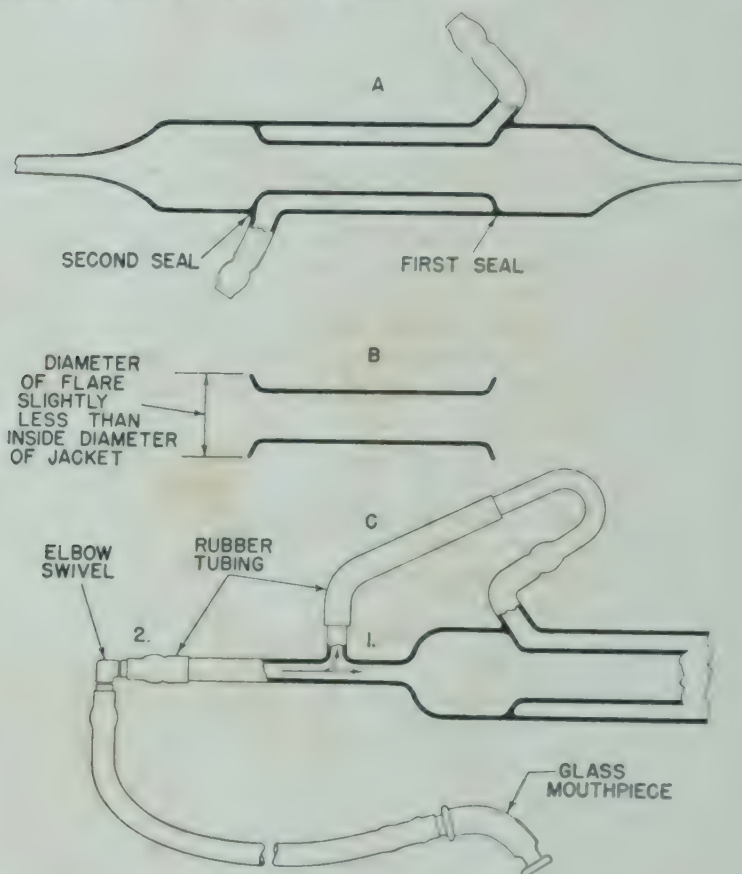


Fig. 49

3. The successful fabrication of the two ring seals is dependent upon the flares which are made on both ends of the inner tube. These flares are made by using a triangular flaring tool. The tube is supported on a double roller and rotated with the palm of the left hand. The end of the tube is heated and spun out to almost a right-angled flare with a wall thickness comparable to that of the tube. The diameter of the flare should be slightly smaller than the inside diameter of the outer tube, Fig. 49B.

4. The flared tube is inserted into the outer tube through the open end. This end is then drawn down and opened. A tube with the form shown in Fig. 49C is butt sealed to the

open end. The two openings are stoppered and a blowing tube is attached to the open point which is held in the left hand. If the tubes are large it is advantageous to use double rollers. The flared inner tube is moved into position by tilting the assembly and the outer tube is heated slowly in a cross-fire or large single jet burner. The tube is rotated until the glass begins to fuse. The seal is effected

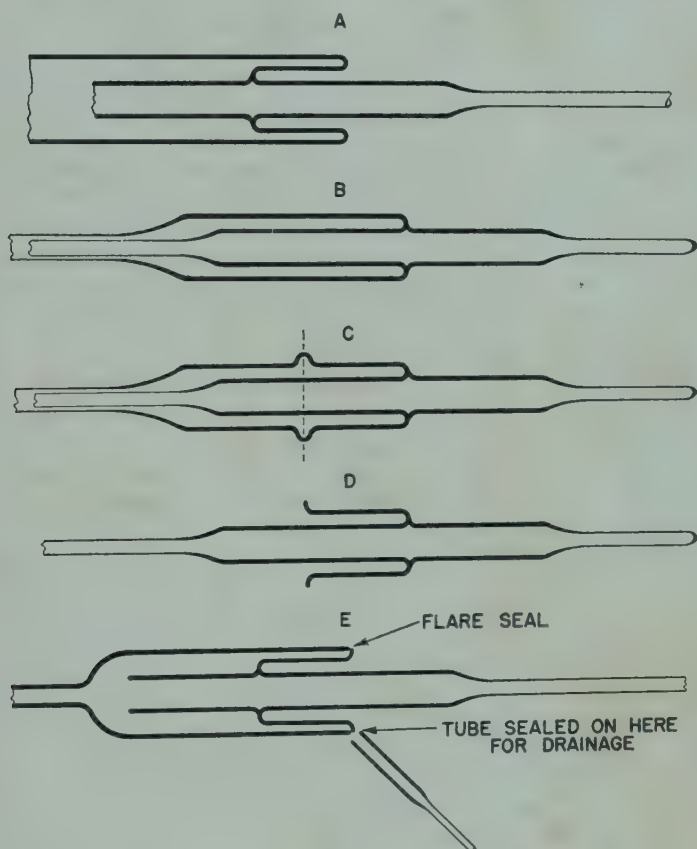


Fig. 50

by using a carbon tool and pushing the fused glass against the edge of the flare. The seal is made with a minimum of collapsing and expanding the glass so as not to disturb the symmetry of the outer tube. The seal is completed by fusing the glass sufficiently, blowing out the glass slightly and smoothing the surface with a flat carbon tool.

5. The side arm is sealed to the outer tube at the edge of the ring seal while the latter is kept hot by periodically heating the assembly. The seals are then annealed and allowed to cool.

6. The condenser is then turned end for end and the open point end is closed by fusing the glass. The side arms

of the condenser and the tube handle on the other end are connected with rubber tubing and a blowing tube is attached at the end, Fig. 49C. The ring seal is completed and the side arm is butt sealed to the outer tube by the procedure used in making the first ring seal.

THE INVERTED RING SEAL

The inverted ring seal is useful when glass jets are required in the production of glass apparatus. The design Fig. 50A shows the two principal seals required in making the inverted ring seal.

1. A tube is drawn to a point. This tube is opened on the opposite end as illustrated in Fig. 41A. An inner tube is made as described in Fig. 41 except that a point is drawn on both ends. The inner tube point actually is centered to a certain degree by permitting it to extend into the point of the outer tube. The seal is completed as previously described, Fig. 50B.

2. The outer tube is then heated with rotation at a predetermined point and a small shoulder is blown, Fig. 50C.

3. The shoulder is allowed to cool until the glass becomes rigid and is then heated while it is rotated with a pin point burner flame at the position indicated by the dotted line. The fused glass is blown out into a thin wall and the glass is scraped away to leave a rough unfinished flare. The flare is carefully heated and spun to an even circular end with a triangular flaring tool, Fig. 50D.

4. The flare is then sealed to the outer tube. In this operation, the heat required to make the seal is sufficient to cause some deformation of the center tube, which is restored to its original shape after the seal is completed. A side arm may be sealed to the assembly if it is required, Fig. 50E.

CHAPTER IV.

TUBE BENDS

The fabrication of parts of glass equipment or assemblies containing sharp or sweeping tube bends requires a technique that is not developed in working with straight tubes. Practice in tube bending is recommended especially in the production of short right-angled bends.

Large sweeping bends are made without difficulty by using the ribbon burner. A mixture of air and gas provides sufficient heat to work Pyrex up to 18 mm. in diameter. The burner may be adjusted to heat tube lengths to 18 inches or more depending on the size of the burner. The tube is heated over the desired length by rotating it in the ribbon burner flame. When the glass is sufficiently softened, it is removed from the flame and the bend is made. No air pressure need be applied into the tube during the bending operation. Mandrels of different sizes are often convenient for making standard sized bends.

The production of short right-angled bends is more difficult than making large sweeping bends. Several characteristics of partly fused glass must be borne in mind when short bends are made. If a bend is made by holding the glass tube at an angle with the vertical, a slight twist will be obtained because of the flow of glass with gravity, Fig. 51A. The fused glass will tend to collapse when a bend is made and, if air pressure is not applied at the right time, a tube with the form shown in Fig. 51C will be obtained. If an unsufficient length is heated, the bend will be too sharp and a kink will be formed, Fig. 51D. These imperfections in a bend will render it almost useless because of the danger of breaking under a small stress. The procedure in making a strong and neat sharp bend is outlined in the following steps:

1. The end of the tube which is held in the left hand is closed with a stopper. The tube is rotated in the burner flame until a section about two diameters in length is fused and slightly constricted because of the flow of glass.
2. The tube is removed from the flame and held in a vertical position with the section held in the right hand above the fused section. The other end of the tube is then moved slowly toward the horizontal with the left hand while air pressure is applied to the open end of the tube. The air pressure is released after the bend is completed and before the sides of the tube begin to bulge.
3. If the sharp bend is examined at this point, one will notice that a certain portion of the inner part of the bend has a heavy wall. The flame is directed over the entire

inner part of the bend and the glass is worked to a uniform wall thickness by repeated expanding and collapsing.

A second bend which is frequently used is the right-angled bend with a radius of curvature of twice the diameter of the tube.

1. The tube end held in the left hand is closed with a stopper. The tube is then uniformly heated over a length of about three diameters.

2. When the glass becomes pliable but not fused to the extent that the tube is constricted, the bend is made by holding the tube vertical and bending the glass below the fused section to the horizontal. Air pressure is applied to

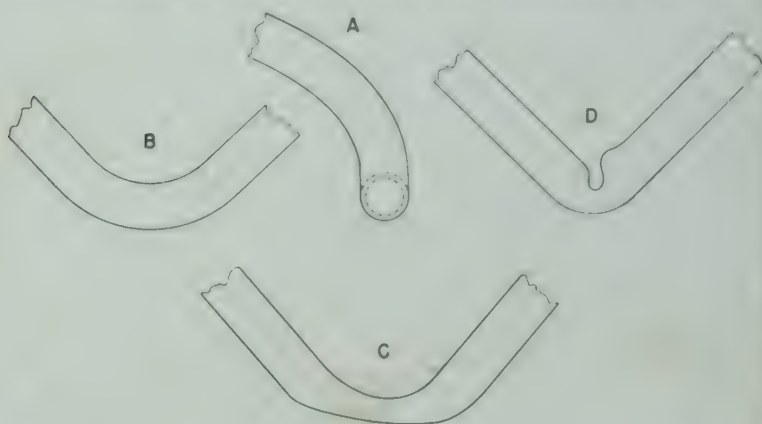


Fig. 51

keep the glass from collapsing or kinking. If the bend is made correctly no additional work is necessary except annealing the glass.

CHAPTER V.

SPIRALS

The fabrication of spirals from glass tubing requires less skill than one would suppose. In small tubing, the ratio of wall thickness to diameter is greater than that of large tubing; and consequently it is only with tubing of larger diameters that more care must be taken in making spirals. Longer sections must be softened by large bushy flame and the tube must be carefully bent into form or wrapped around the mandrel, so that the tubing is not appreciably flattened.

A 40" length of tubing with 1-mm. wall thickness and 3-mm. bore (5-mm. outside diameter) is best used for the first exercise in making spiral. One end of the tube is closed with a stopper.

1. This tube is bent sharply at a right angle about 6" from the open end; position 2, Fig. 52A. This length is to serve as an end of the spiral.

2. The tube is then heated at position 4, Fig. 52A, and bent toward the operator in another right-angled bend, the distance 2 to 4 being the radius of the spiral.

3. The tube length 4 to 3, Fig. 52B, is required for the fabrication of the spiral. From the proposed coil diameter, the length of glass required for the completion of the spiral can be calculated. The section 1 to 2 is held in the left hand at an angle and heated in the burner flame, while the long section 4 to 3 is supported with the right hand. A portion of the tube is heated near 4, Fig. 52C, by both rotation and a movement along the axis of the tube. The major portion of the heating should always be on the outer side of the tube.

4. As the glass becomes plastic, section 1 to 2 is held horizontal and section 4 to 3 is bent slowly to form the section of the circular bend for the first spiral, Fig. 52B.

5. The tube is then heated beyond the bent portion until the glass is softened. This section of the tube is formed into an arc of the circle previously started. This step is repeated until the first turn is completed. All bending is done outside the flame and observation from different angles will assist in the alignment of the tubing.

6. After the first complete circle is made truly axial to the tube section 1 to 2, further turns are made much more easily because the softened section is always bent into coincidence with the outline of the turn below it, Fig. 52D. The spacing between successive turns should be constant as shown in the side view of Fig. 52D. Spirals are

often required as the inner tubes of condensers and therefore the ends must be aligned as section 1 to 2 of Fig. 52D. The tube ends are flared sufficiently so that good ring seals can be made.

More precision is possible in the fabrication of spirals by using a mandrel for forming the glass. Various sizes

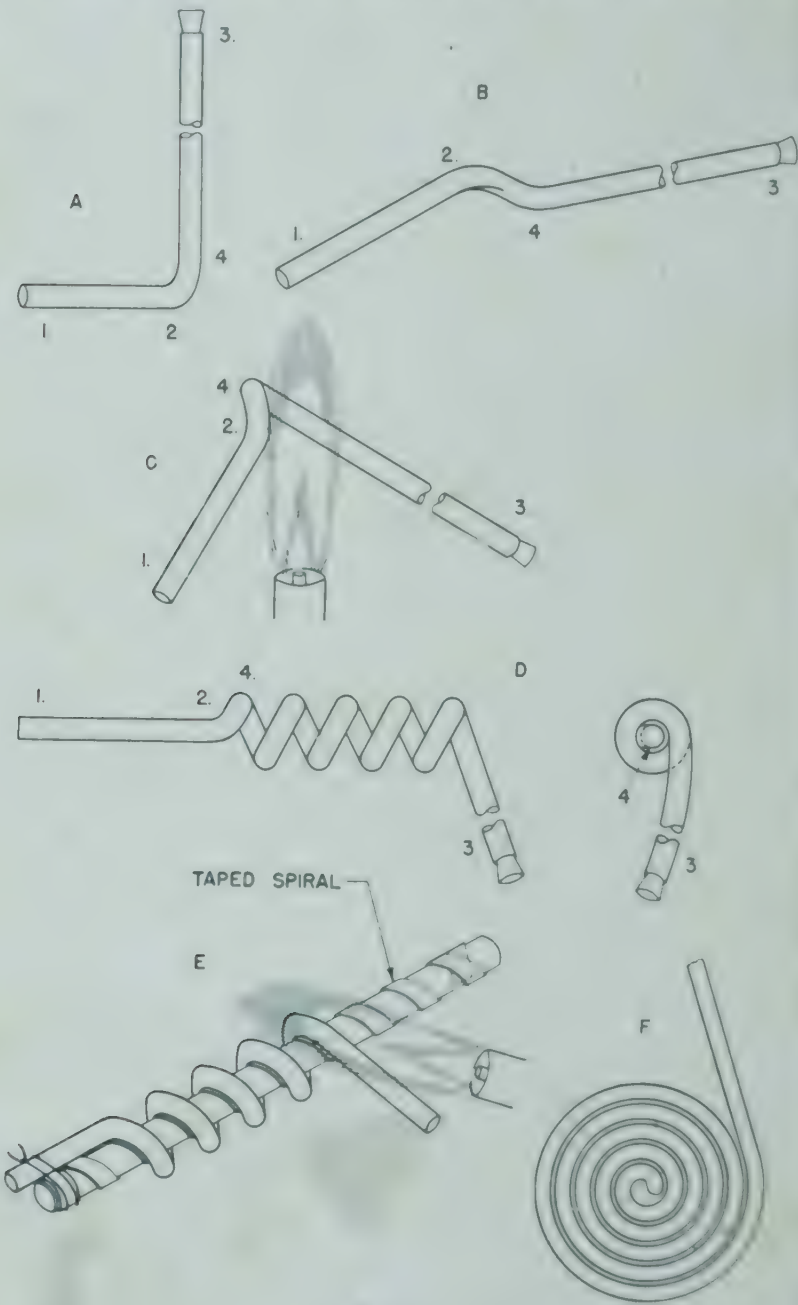


Fig. 52

of mandrels can be made of metal pipes which are suitably mounted, but a great deal of success has been obtained in using glass tubing. The glass-tube mandrel is simply a glass tube wrapped spirally with asbestos tape.

1. The tube is heated at a section about 6" from one end and bend in a right angle. This tube is tied to the wrapped mandrel, Fig. 52E. The glass is then heated in short sections of about 1" in length and the tube is wrapped around the asbestos-covered glass mandrel. The tape serves as a guide for the spacing of the spiral turns.

2. The spiral and mandrel are allowed to cool and the former is removed by wetting the tape with water.

The flat spiral, Fig. 52F, is sometimes required in the fabrication of glass equipment.

1. A required tube length is heated at a section 6" from one end. The glass tube is bent in a short right angle.

2. The glass is then heated at the right angle and the inner turn of the spiral is started by bending the tube in a circle around the short section that is used as a handle.

3. The spiral is continued by repeatedly heating short sections of the tube and bending it around the inner spirals.

4. After the flat spiral is completed, the tube is cut away at the center of the spiral with the burner flame.

CHAPTER VI.

CLOSED GLASS TUBING CIRCUITS

Close observation of fabricated glass apparatus will show that unnecessary seals in conspicuous places detract from the appearance of the finished equipment. There was a time when it was necessary to make extra seals in glass equipment because of the high coefficient of expansion of soft glasses. No amount of speed could overcome fractures in attempting to complete two or more seals in one operation. Now, owing chiefly to the rugged shock-resistant qualities of Pyrex brand glass #774, it is possible and often convenient to assemble any number of parts.

One important thing must be remembered in making closed glass tube circuits: when two or more seals are made at the same time, each must actually be partly completed. Instead of fusing the glass so that it will just stick together when one glass tube is pressed against the other, the opening in the glass is heated until it is fused to yield a butt seal which requires only work in making the seal smooth. This seal may be left as one performs the same operation at another point in the circuit. When the circuit is completed, each seal can be worked until smooth without the danger of fractures at the seal.

An illustration of closed circuit seals is given in Fig. 53A.

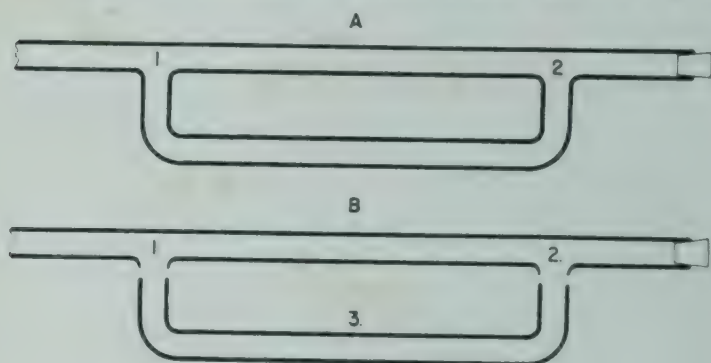


Fig. 53

Seals of this nature are necessary for the fabrication of McLeod gages, manostats, flowmeters, etc.

1. The straight tube, Fig. 53B, is opened at points 1 and 2 by fusing the glass and blowing it out in the steps outlined for preparing an opening in the wall of a tube.

2. The second tube is bent at right angles at each end. The glass at each end is then cut with the burner flame and each end is slightly flared, Fig. 53B, tube 3.

3. The end of tube 3 and the opening at 2 are heated until the glass begins to fuse sufficiently to give a leak-proof seal when the two are pressed together.

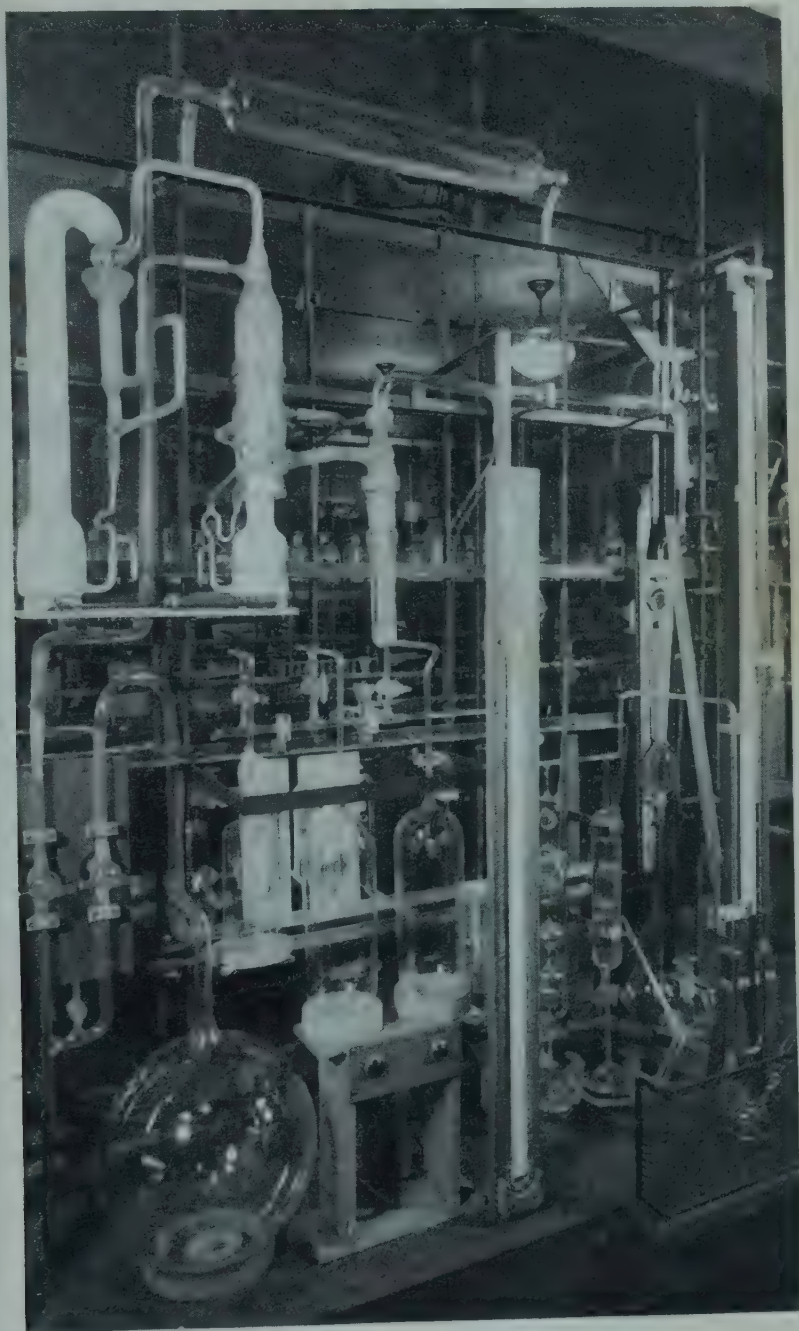


Fig. 54

4. The seal at position 1 is then started. The main difficulty which will be encountered at this point is to fuse the glass around the entire circumference of the openings. This is necessary or small pin-holes will be formed because of uneven heating. After the fused glass is pushed together, the seal is completed by the procedure recommended for a side tube seal. The glass is then annealed.

5. The first seal is warmed slowly and is completed by the technique of making side seals. The glass is carefully annealed after the seal is smooth.

Regardless of the shape of the parts to be joined, the only critical factors are the positive matching of tube openings and production of partial seals which are flowed together by pushing together the two fused ends.

TORCH SEALING

All glass equipment which is mounted on racks must frequently be built in several sections or parts, each of which must be sealed in place on the rack. Hand torches instead of the bench burner must be used. The glass is heated by moving the hand torch flame around the glass tube ends. It is just as important to develop the skill in torching technique where the glass is uniformly heated around the glass tube as is the rotation of glass in the burner flame in hand work. The flame is kept perpendicular to the glass tubes and is moved completely around the circumference. Overlapping or underlapping in the heating is not permissible. Overlapping creates a hot spot in the glass which is more easily blown when pressure is applied, and underlapping will leave a partially fused section which cannot be worked satisfactorily.

A good deal of planning is necessary when an intricate glass assembly is to be mounted on a rack. One important thing to remember is that seals are more easily made when the glass tubes are in a vertical, rather than a horizontal position; and seals so made are superior, both in appearance and durability. All bends should be smooth and the tubes should be positioned for an adequate number of clamps. All glass parts should be so placed that a torch can conveniently be used if repairs are necessary. An example of a neatly arranged assembly is shown in Fig. 54.

The procedure in making a vertical tube seal is illustrated in Fig. 55. The operation has been simplified for convenience of description. In actual practice the two tubes could be ends of two separate glass assemblies.

1. The ends should be perfectly square. The upper tube is clamped rigidly on the rack and has a blowing tube attached at some convenient point. The bottom tube is closed with a stopper and is held or loosely clamped directly under

the upper tube. A gap of about $1/16''$ is left between the tubes, Fig. 55A.

2. The two ends are heated by moving the hand torch flame around the tubes until the glass is fused but not appreciably deformed. The bottom tube is then lifted until a complete contact is obtained around the circumference of both tube ends. The glass is allowed to cool slightly. The glass just above the temporary seal is heated by moving the torch flame around the tube. As the glass begins to fuse the lower tube is pushed upwards until sufficient glass is gathered to give a thickened circular band around the tube, Fig. 55B.

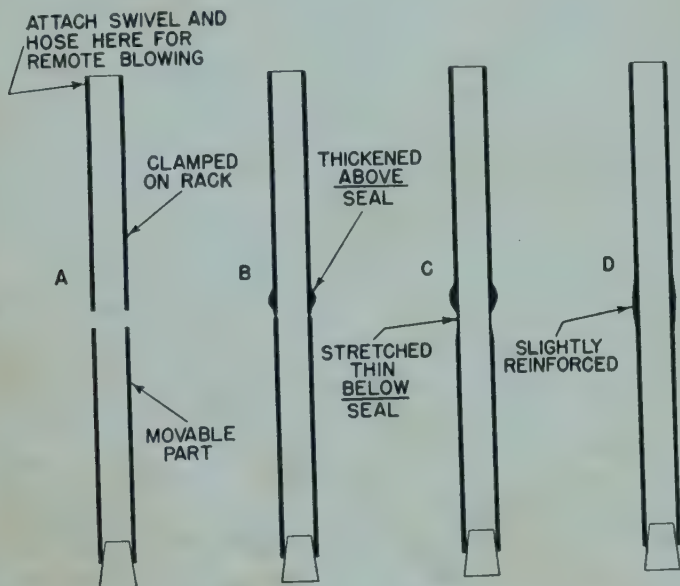


Fig. 55

3. The glass is allowed to cool until it supports the weight of the lower section. The glass tube assembly is then heated uniformly just below the seal and drawn to a thin wall, Fig. 55C.

4. The seal is then completed by heating the thickened and thin sections at the same time. As the glass is fused and worked, the glass in the thickened portion will gradually flow with gravity and when the seal is completed it has the form as illustrated in Fig. 55D. The tubing is slightly reinforced at the seal.

The Litton hand torches described and illustrated in Chapter I are recommended for sealing tube assemblies. The larger torches are useful in sealing tubing with large diameters.

Vertical capillary seals should be made by using a small Hoke Jewel torch by the procedure as described for ordinary tube seals. The inside bore should be perfectly aligned when first contacted. The seal should be completed with a minimum of enlargement of the bore by blowing.

Horizontal seals on fixed tubes cannot be made by fusing the glass around the circumference of the attached tubes because the glass will flow with gravity. The only procedure which is recommended is the spot fusing technique. The glass is fused and the tubes are pushed together. The rough seal is allowed to cool until the glass becomes rigid. The seal is then completed by successively fusing short segments of the circumference and working each until the glass is smooth. Each completed portion is allowed to cool before the next is fused.

No matter how careful one may be, there are times when small pin-holes appear on a torch seal. The only satisfactory way the hole can be closed when the tubing is clamped in position, is to spot a small amount of fused glass over

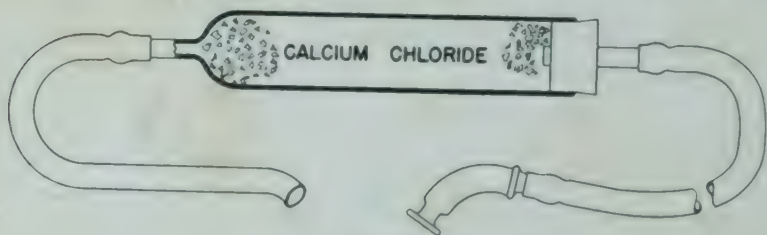


Fig. 56

the opening. A small, thin glass rod is used. The glass at the end of the rod and that at the seal are fused sufficiently so that the glass will stick when touched to the tube. The rod is then cut by the burner flame as close to the seal as possible. The seal is then worked until the glass is smooth.

If instead of a pin-hole a small gap develops at the seal which cannot be closed by spotting with a glass rod, a thin glass ribbon can be spotted over the opening. The ribbon is made by flattening a fused glass rod with a forceps and then fusing the flat glass and pulling it to a glass ribbon.

When seals are made on a vacuum system or on a complex gas reactor system, it is always advisable to use a drying tube with the blowing tube, Fig. 56. Any suitable desiccant which will eliminate moisture is satisfactory.

Cutting out or removing sections from an all-glass system is a delicate operation. If the tubes are small and flexible the glass can be cut by first marking the glass with a file, wetting the mark and breaking the tube by the procedure outlined in the first chapter. However, on tube sizes above 18 mm. it is necessary to make a file mark about a quarter-

inch long. The end of a glass rod is heated until the glass begins to flow and is immediately touched to the center of the mark after the latter is wetted with water. Usually, the expansion of the tube caused by the heat from the hot rod will cause a crack that will encircle the entire tube. If the crack does not completely encircle the tube, it may be led in the proper direction by touching the point of a hot glass rod about $\frac{1}{4}$ " beyond the end of the crack. If the crack breaks away and begins to run lengthwise in the glass of the tube, it must be stopped before another attempt is made to break the tube. The extension of the crack is stopped by slowly warming the tube beyond the end of the crack. As the temperature of the tube increases, the flame is brought closer to the cracked area. The glass will fuse together if it is not heated too rapidly.

ELECTRONIC WELDING OF GLASS

Hand torches or blast burners when used in sealing heavy Pyrex tubing or pipe have one principal disadvantage. The glass is heated through the surface and, to fuse the tube end sufficiently for sealing, portions of the surface are often overheated. Volatile constituents of the glass are lost because of the high temperatures in the glass surface.

Electronic heating is becoming important for internal heating. This form of heating glass has been performed with high-frequency current through dielectric loss between capacitor plates or by the use of special gas-flame conducting electrodes. The latter method of internal heating is described by E. M. Guyer.¹

Gas-electrode sealing is comparable to resistance welding. The gas-flames at the tips of the electrodes have two principal functions:

1. The glass is preheated to a temperature where it ceases to be an insulator and becomes a conducting medium.
2. The flames provide a conductive path for the heating current.

The technique of using these electrodes is similar to the torching technique previously described. The flames are directed against the glass and the temperature is regulated within the glass by increasing or decreasing the distance between the glass and the tip of the electrode.

Since radio high-frequency generators are expensive, investment in such equipment would be warranted only when considerable work is done on equipment requiring internal heating.

¹E. M. Guyer, *Electronics*, Vol. 18, No. 6, 1945, page 92.

CHAPTER VII.

GROUND SURFACES FOR GLASS APPARATUS

The importance of ground glass joints, stopcocks and equipment containing ground glass surfaces can readily be visualized by inspecting a research laboratory. An inventory of all glass equipment will show that without stopcocks and ground joints the workers would encounter difficulty in the handling of gases and liquids. Certain basic equipment units when fitted with stopcocks and ground joints have been planned and constructed so that they can be altered for different uses by merely changing the auxiliary unit parts. Ground joints are ordinarily used in systems where it is desirable to remove parts of the total glass assembly for cleaning and for charging or removing liquids or reactants. They are also used as simple connectors between large and intricate parts of a glass reactor system, or as closures for volumetric glassware and reagent bottles. Stopcocks are used for controlling and directing gas traffic in closed glass systems or in controlling the flow of liquids.

The history of the development of stopcocks and ground glass joints need not be discussed. Producers of glass equipment and individual glass blowers developed techniques which improved from a clumsy cone and socket to a precise unit indispensable in the production of modern laboratory equipment. It is interesting to note that the development of various laboratory techniques, among which vacuum technique was the most important, actually required that joints and stopcocks should be leak-proof. Another development which influenced the production of more flexible laboratory equipment was the standardization of some joints and stopcocks. Under the guidance of the National Bureau of Standards, a standard taper was voluntarily established by mutual consent of producer, distributor and the consumer. Joints and stopcocks made according to the specifications set forth in Commercial Standard CS 21-39¹ are interchangeable. These are stamped with the standard taper mark combining the letters S and T (see Fig. 71). No definite type of glass is specified for the production of the standard joints and stopcocks. The general requirements given in CS 21-39 are as follows:

1. All interchangeable joints, stopcocks and stoppers shall have a taper of 1 ± 0.006 mm/cm of length on diameter.
2. All joints, stopcocks and stoppers shall be made with standardized working tools checked with gages certified by the National Bureau of Standards.
3. All master gages used in the production of interchange-

able joints, stopcocks or stoppers must be made of tool steel, hardened and ground.

The detailed requirements for joints, stopcocks and stoppers are also given and Commercial Standards CS 21-39 should be consulted if information is required.

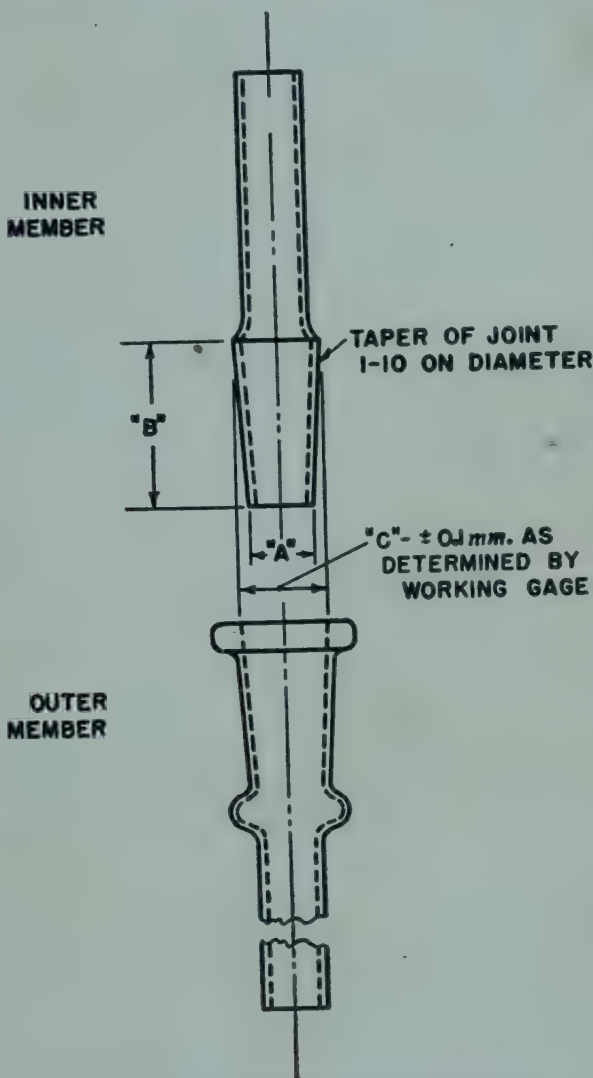


Fig. 57. (Drawings by Richard P. Jones, Gulf Res. & Dev. Co.)

GROUND JOINTS

The standard ground joint is shown in Fig. 57. The inner and outer members of the joint have a tubing diameter which corresponds approximately to the outside diameter of the small ground end of the inner member of the joint. Due to this tube-size ratio, small joints when sealed to large

flasks appear ridiculously fragile and out of proportion. Large tubing cannot be sealed close to the joint because of the danger of warping the ground surface. It is advisable, however, to butt seal larger tubing to the outer member at a point approximately $\frac{3}{4}$ " from the joint so as to offer some protection to the flask by having a larger tube sealed to it. With such an arrangement a break in the small tubing of the joint will not damage the flask.

The ground joint may be obtained with a ground section in one of three different lengths. The full-length ground joint which is the most popular is made in sizes ranging from 5 to 71 mm. approximate diameter at the large end of

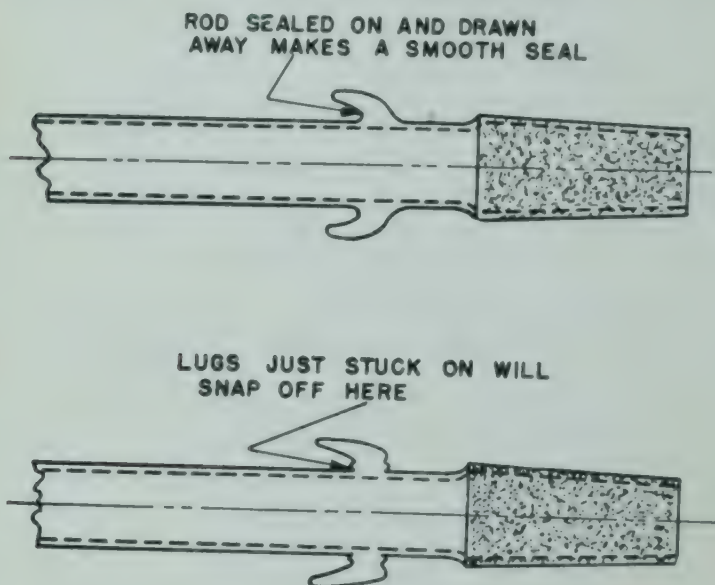


Fig. 58

the ground zone. The medium-length joint sizes are from 5 to 40 mm., while the short-length joints range from 10 to 71 mm. The standard dimensions for all three joints are given in Table 4. The listed sizes correspond to two dimensions of the joint. The first number indicates the approximate diameter in millimeters of the large end, the second gives the length of the ground glass zone. The taper is 1 to 10 with the tolerances within ± 0.006 mm./cm. length on diameter.

The complete taper joint may be purchased with four tying lugs or hooks by which the joint can be held together with rubber bands or small springs. If the hooks are required, they must be specified when joints are purchased. On occasions it may be necessary to attach hooks on plain joints. The following procedure is recommended:

1. In operations where it is necessary to heat the glass sufficiently to fuse and flow the two glass parts together, one is sometimes hindered by the bright glare of the yellow sodium flame. Didimium or Neophan spectacles or goggles are recommended to filter out the sodium glare and allow visibility in all operations where the glass is heated. A 5 mm.-diameter glass rod is used in making the hook. The end of the rod and the tube are heated until the glass is fused sufficiently to flow together when the two fused surfaces are contacted. If the glass is not heated sufficiently and the lugs are attached as in Fig. 58B they will snap off under strain.

TABLE 4—SPECIFICATIONS AND DESIGNATIONS FOR STANDARD TAPER INTERCHANGEABLE GROUND JOINTS
(Taper, 1 to 10; i.e., one mm. \pm 0.006 mm. per centimeter of length on diameter)

Designation (Large Diam./ Length of Ground Zone)	Computed Diam. Large End of Ground Zone	Approx. Diam. Small End of Ground Zone
mm.	mm.	mm.
FULL-LENGTH JOINTS		
5/20	5.0	3
7/25	7.5	5
10/30	10.0	7
12/30	12.0	9
14/35	14.5	11
19/38	18.8	15
24/40	24.0	20
29/42	29.2	25
34/45	34.5	30
40/50	40.0	35
45/50	45.0	40
50/50	50.0	45
55/50	55.0	50
60/50	60.0	55
71/60	71.0	65
MEDIUM-LENGTH JOINTS		
5/12	5.0	3.8
7/15	7.5	6.0
10/18	10.0	8.2
12/18	12.0	10.2
14/20	14.5	12.5
19/22	18.8	16.6
24/25	24.0	21.5
29/26	29.2	26.6
34/28	34.5	31.7
40/35	40.0	36.5
SHORT-LENGTH JOINTS		
10/10	10.0	9.0
12/10	12.0	11.0
14/10	14.5	13.5
19/10	18.8	17.8
24/12	24.0	22.8
29/12	29.2	28.0
34/12	34.5	33.3
40/12	40.0	38.8
45/12	45.0	43.8
50/12	50.0	48.8
55/12	55.0	53.8
60/12	60.0	58.8
71/15	71.0	69.5

The glass must be smoothly flowed together as shown in Fig. 58A. The glass rod, after it is attached, is bent back parallel to the glass tube, drawn out, and cut off in the burner flame.

SPHERICAL GROUND GLASS JOINTS

Another type of ground glass joint which finds use in fabricating scientific glass apparatus is the ball and socket or spherical joint. These joints lessen the risk of breakage because they need not be perfectly aligned as in the case of taper joints. If spherical joints are lubricated properly they may be moved when the system to which they are sealed is

TABLE 5—BALL-AND-SOCKET GROUND GLASS JOINTS

Size Designation	Diam. of Ball, mm.	Approx. I.D. of Tube, mm.
*12/1	12	1
*12/1½	12	1½
*12/2	12	2
12/3	12	3
12/5	12	5
18/7	18	7
18/9	18	9
28/11	25	11
28/12	25	12
35/20	35	20
35/25	35	25
50/30	50	30
65/40	65	40

Note:—Items marked (*) are made of capillary tubing.

under vacuum. The taper joint has a greater tendency to stick, especially if it is not lubricated properly.

The size of a spherical joint is designated by its number. The first gives the inside diameter of the tubing in millimeters. The second number designates the diameter of the ball. The available sizes of spherical joints are given in Table 5.

It is generally necessary to clamp spherical joints together. Metal clamps are marketed by Ace Glass Company, Inc. Clamp and joint are shown on the right in Fig. 59. Clamp sizes are 12, 18, 35, 50 and 65 and are used with joints with the corresponding ball sizes. Another useful clamp, shown on the left in Fig. 59, is sold by the Arthur H. Thomas Company.

Experience in the laboratory showed that more spherical joints are broken by improper clamping than by any other cause. Some consideration must be shown whenever pressure is being applied to the glass. One should never attempt to seal a leaky spherical joint by increasing the pressure on the joint with the set screws of the clamp. Usually the leak is caused by improper lubrication or by small dirt particles which were not removed before the joint was assembled.

SEALING JOINTS TO GLASS EQUIPMENT

Joints usually are sealed to straight tubing or flasks, and before the joints are sealed, they should be cleaned thoroughly. A small reagent bottle of carbon tetrachloride, chloroform or benzene should be kept on the reagent shelf for cleaning joints and stopcocks. A small glass holder wrapped with asbestos tape is pressed into the joint and the latter is aligned for minimum wobble during rotation. The joint is sealed to straight tubing by the simple butt sealing technique. Round-bottomed flasks can be purchased with attached joints but sometimes it is necessary to replace a broken joint or to seal a joint to a balloon flask which has the conventional opening. Flask holders, obtainable from various companies which supply glass-working equipment, come in various sizes and are simple in design. Four metal bands

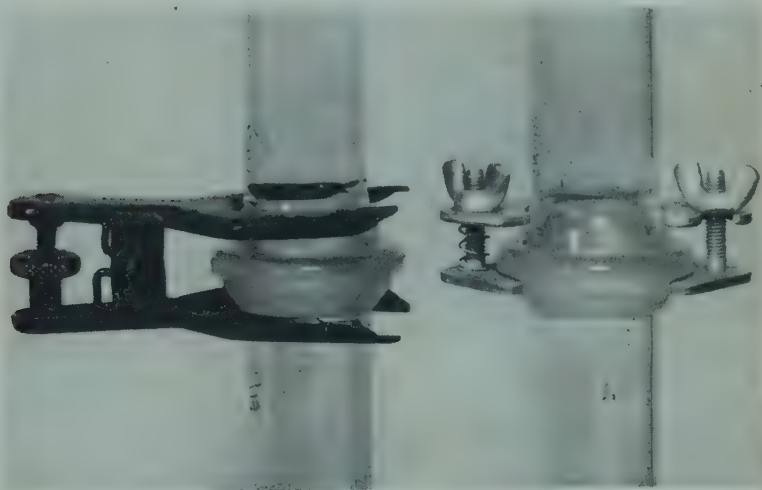


Fig. 59

or flexible rods are attached to one end of a round handle. These bands or rods which are 90° apart extend around the flask and are held against the latter by the tension in the rods, or by a wire coil spring which is hooked under each end of the bands. The flask can then be held in one hand and rotated during the sealing process. The procedure for preparing the opening in the flask will depend on the tubing size of the neck: usually between $\frac{1}{2}$ " and 2". The neck is either cut and used as such or it must be drawn down to the diameter of the joint tubing. Simple butt sealing, of equal-diameter tubes and of tubing of different sizes, has been described and the same procedure can be used here. Some practice in balancing and rotating the flask is required, especially if the flask is large. Large flasks must be supported on the rollers.

Adapters which consist of two different sized joints (inner

joint of one size sealed to the outer joint of another size) are sometimes needed. Any combination of sizes can be made by butt sealing two different joint parts together.

STOPCOCKS

Stopcocks of simple or special designs are made up in two parts. The shell or barrel—the outer member to which are connected the outlet tubes—has a tapered inner ground surface. The second part—the ground plug or inner mem-

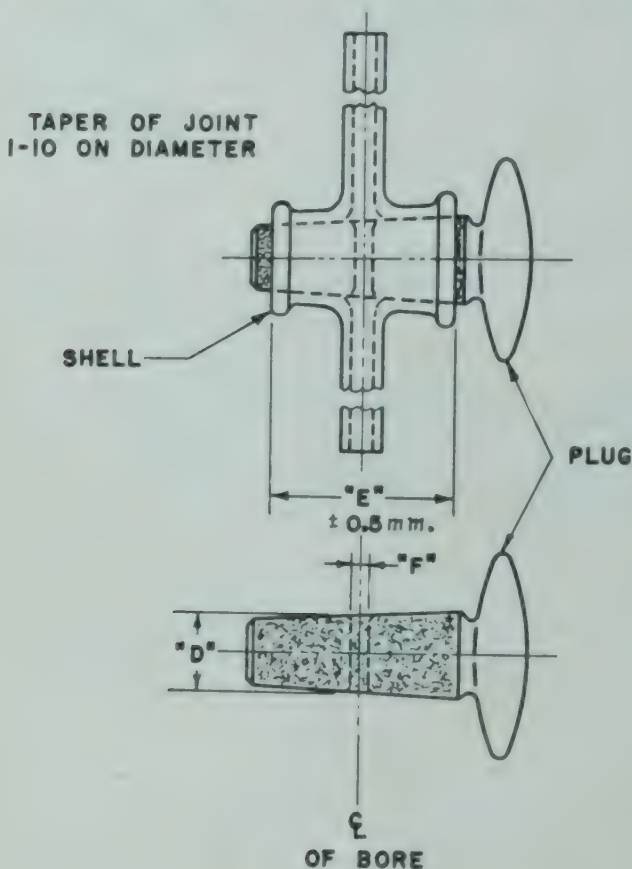


Fig. 60

ber—fits into the barrel. The plug is drilled so that the bore hole serves as a connecting link between the respective outlet tubes.

The standard straight-bore stopcock is described, and the production requirements are given in Commercial Standards CS 21-39. It is shown in Fig. 60. The taper of the barrel or shell is $1 \pm 0.006 \text{ mm./cm.}$ on diameter (1-10). The number, diameter of plug at the center line of the bore hole, length of shell and diameter of the bore hole in the plug of

the various sizes of the standard straight bore stopcock are given in Table 6. The manufacturers of this stopcock have added one improvement by grinding a groove in the small end of the plug for retaining keys or rubber rings. This standard stopcock is not recommended for vacuum apparatus or liquids with low densities.

Many other forms of stopcocks available from various manufacturers are not standardized. The frequently-used oblique-bore stopcock is supplied with a single bore, or double bore for a three-way stopcock. The tee or 120° types have three outlet tubes and are useful for gas traffic control. Numerous innovations, such as plugs with outlets through the small end or mercury seal cups, have been incorporated in stopcocks. In *Bureau of Standards Circular C 430*, Martin Shepherd² has attempted to stir the imagination of the laboratory technician in designing single stopcocks which take the place of several conventional single-bore types.

Sealing Stopcocks to Glass Equipment

Stopcocks are sealed to glass equipment by using the simple butt-sealing technique. Three things should be kept in mind when seals are made:

1. The stopcock plug is removed and the barrel cleaned thoroughly to remove all grease.

TABLE 6—STANDARD DIMENSIONS FOR INTERCHANGEABLE STRAIGHT-BORE GROUND-GLASS STOPCOCKS

Standard Stopcock Number	Diameter of plug at center line of bore	Length of shell ±0.5 mm.	Diameter of bore hole in plug
	<i>D</i>	<i>E</i>	<i>F</i>
	mm.	mm.	mm.
1	12	30	1
1½	12	30	1½
2	12	30	2
3	17	40	3
4	17	40	4
5	20	44	5
6	20	44	6
8	25	52	8
10	35	56	10

2. The open ends of the barrel are plugged with corks. Since it is necessary to balance the stopcock, one should use corks of the same size. The larger opening in the barrel is closed by inverting one cork and pushing the large end of it into the barrel so that both corks are about equidistant from the outlet-tube center line.

3. The seal must not be made close to the stopcock barrel.

Experience has shown that at least $\frac{3}{4}$ " should be allowed between the barrel and the seal.

The stopcock is sealed to glass tubes or equipment parts by the various techniques previously described. When seals are made by hand in a burner flame, the outlet tube is used as a handle for rotating the stopcock.

PRODUCTION OF STANDARD TAPER JOINTS AND STOPCOCKS

The commercial production of joints and stopcocks has been satisfactory and it is only occasionally that a joint or stopcock which is to be used for routine work in the laboratory must be rejected. There are times, however, when such joints must be repaired by regrinding. Furthermore, the development of the technique in making joints and stopcocks will be helpful when special joints or stopcocks are required which cannot be purchased. Stopcocks for vacuum systems must also be ground to closer tolerances to be satisfactory.

TOOLS REQUIRED FOR MAKING JOINTS AND STOPCOCKS

The tools necessary for the shaping and grinding of glass are shown in Fig. 61. Three sets are shown each of which consists of a standard hexagonal taper reamer, taper grinder, taper grinding sleeve which fits over the taper



Fig. 61

grinder, taper socket and a taper grinding sleeve which fits into the taper socket. The socket on the right was designed for shallow tapers. It is split so that the grinding sleeve can be easily removed.

The standard carbon hexagonal reamers can be purchased from any company which markets glass-blowing supplies. Suitable handles may be obtained for each set. Steel hexagonal taper reamers, which can be made if shop facilities are available, are shown in Fig. 62. They are made of steel and are lightened by boring out the center. These reamers are unbreakable and will not wear. The dimensions for the four standard taper reamers are given in the dimensions log in Table 7. Beeswax should be used as a lubricant when hot glass is worked with the metal reamers.

Grinding tools cannot be purchased but are easily made if machine shop facilities are available. The drawings for the standard long taper grinder and socket with their respective sleeves are given in Fig. 63. The log of the dimensions for three different sets is given in Table 8. The grind-

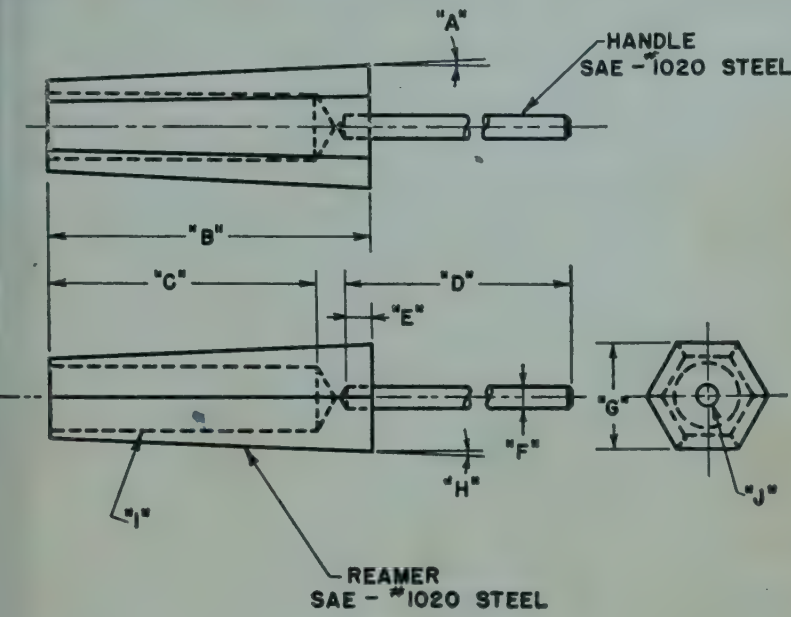
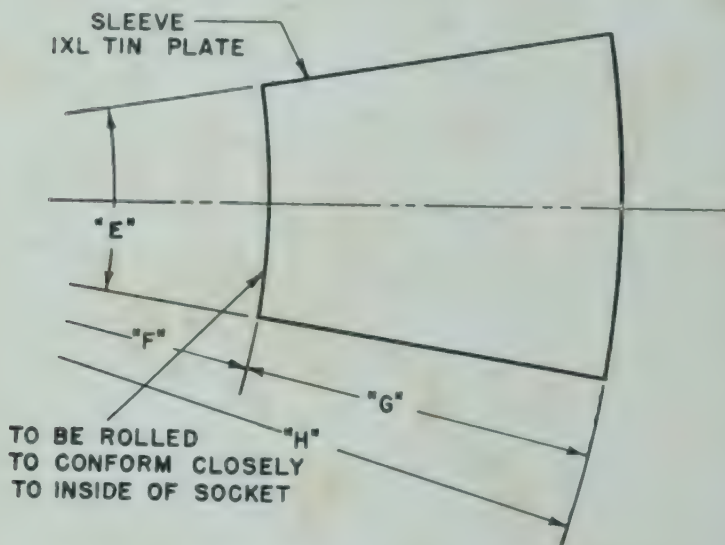
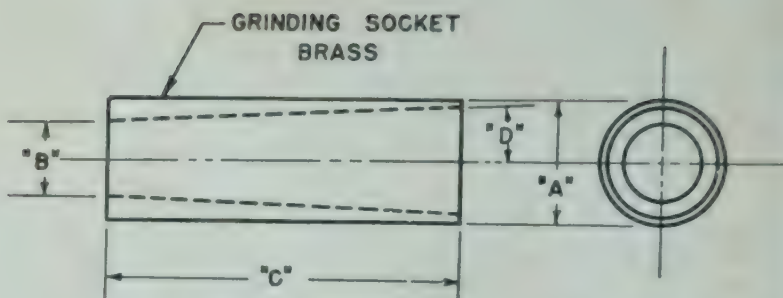


Fig. 62

TABLE 7—STANDARD TAPER REAMER

"A"	"B"	"C"	"D"	"E"
2°52'±2'	6"	—	8"	1½"
2°52'±2'	6"	5"	8"	1½"
2°52'±2'	6"	5"	8"	1½"
2°52'±2'	6"	5"	8"	1½"
"F"	"G"	"H"	"I"	"J"
⅜"	0.625"±0.003"	2°29'	—	⅜"
⅜"	1.088"±0.003"	2°29'	⅜"	⅜"
⅜"	1.543"±0.003"	2°29'	¾"	⅜"
⅜"	2.000"±0.003"	2°29'	1 ¼"	⅜"

ing tools are made of brass with rolled tinplate as sleeves. Basically this set of grinding tools is designed for long tapers and for all the taper sizes between the extreme dimensions. There are occasions, however, when short tools are required. The drawings for this set are given in Fig. 64. A log of all critical dimensions is given in Table 9. This set of grinding tools covers a large range of sizes, the smaller sizes being quite useful in making joints and stopcocks for microchemical equipment. This latter set is made of 18-8



ASSEMBLY

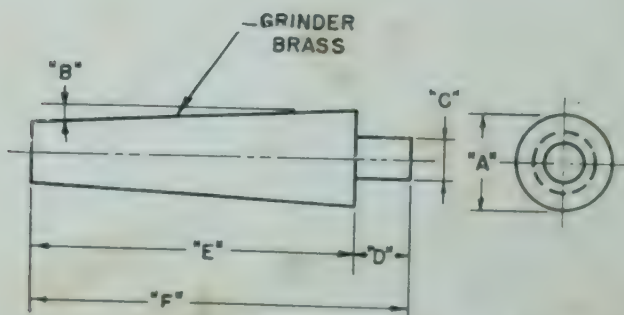
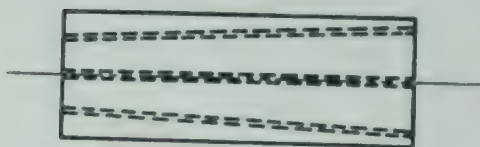
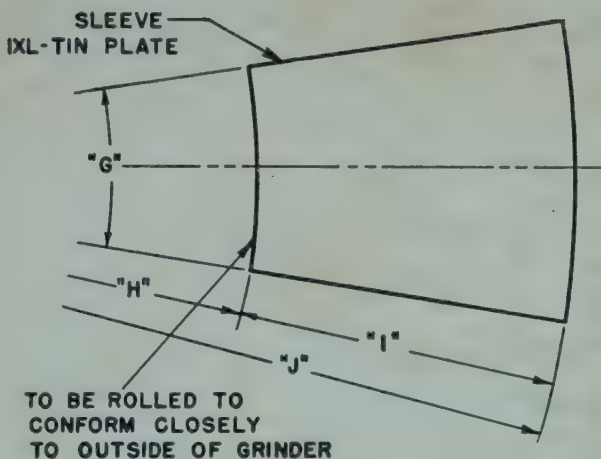


Fig. 63 (Continued)



ASSEMBLY



Fig. 63

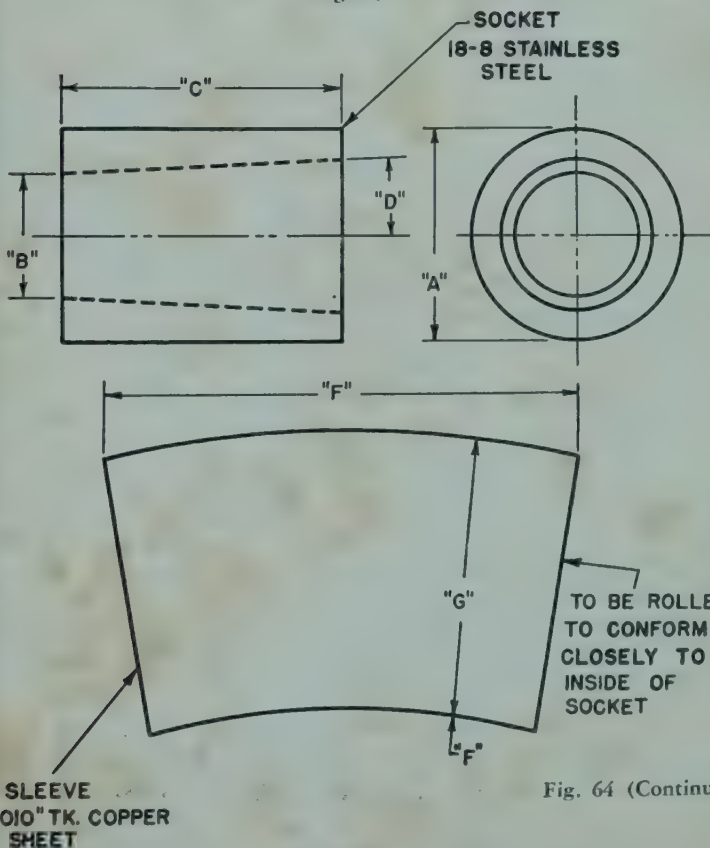


Fig. 64 (Continued)

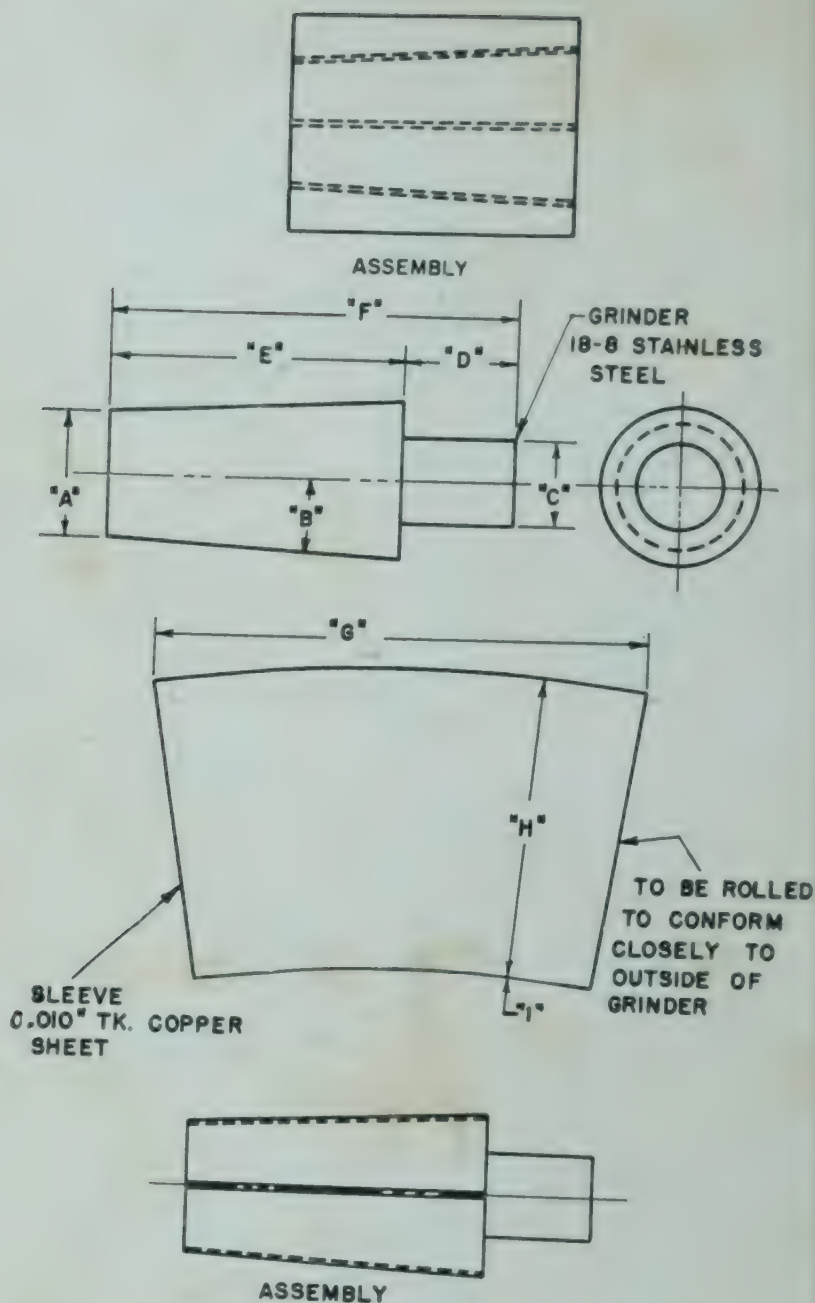


Fig. 64

stainless steel and sleeves for the smaller sizes are made of thin copper sheet.

PRODUCTION OF A STANDARD TAPER JOINT

The most difficult operation in making a joint or stop-cock is the shaping of the glass of both the outer and inner

TABLE 8

STANDARD TAPER GRINDING SOCKET AND SLEEVE
(LONG)*Socket Dimensions*

"A"	"B"	"C"	"D"
1 1/4"	0.375" ± 0.002 "	6"	2°52' $\pm 2'$
1 5/8"	0.8125" ± 0.002 "	6"	2°52' $\pm 2'$
2 1/8"	1.250" ± 0.002 "	6"	2°52' $\pm 2'$

Sleeve Dimensions

"E"	"F"	"G"	"H"
18°	3.75" ± 0.010 "	6.007" ± 0.010 "	9.757" ± 0.010 "
18°	8.125" ± 0.010 "	6.007" ± 0.010 "	14.132" ± 0.010 "
18°	12.5" ± 0.010 "	6.007" ± 0.010 "	18.507" ± 0.010 "

STANDARD TAPER GRINDER AND SLEEVE (LONG)
Grinder Dimensions

"A"	"B"	"C"	"D"	"E"	"F"
0.9375" ± 0.002 "	2°52' $\pm 2'$	3/4"	1"	6"	7"
1.375" ± 0.002 "	2°52' $\pm 2'$	3/4"	1"	6"	7"
1.8125" ± 0.002 "	2°52' $\pm 2'$	3/4"	1"	6"	7"

Sleeve Dimensions

"G"	"H"	"I"	"J"
18°	3.368" ± 0.010 "	6.007" ± 0.010 "	9.375" ± 0.010 "
18°	7.743" ± 0.010 "	6.007" ± 0.010 "	13.750" ± 0.010 "
18°	12.118" ± 0.010 "	6.007" ± 0.010 "	18.125" ± 0.010 "

members. A certain amount of glass must be gathered for building up the wall thickness in the sections that are ground. If the wall thickness is not increased the joint will be quite fragile because of the grindaway of glass. The required tools for making a joint or stopcock are a standard taper scale, Fig. 65C, three calipers, a standard taper reamer, a round carbon tool, a flat carbon tool, standard taper grinding socket with two sleeves, a standard taper grinder with two sleeves, grinding carborundum grit numbers 220, 320, 600 and Turkish emery SF-10.

As an example, suppose a size 24/40 joint is to be made. From the detail requirements given in Table 4 the glass tubing must have an approximate diameter of 20 mm. The inner member when finished has a ground section 40 mm. long. The diameters of the ground sections at the small or open end and the large end are 20 and 24 mm. respectively. The procedure for making the joint is as follows:

1. The outer member will be made first. A 14" section of approximately 20 mm. tubing is chosen from stock and two points are drawn on each end. The point held in the right

TABLE 9
STANDARD TAPER GRINDING SOCKET AND SLEEVE
(SHORT)

Socket Dimensions

No.	"A"	"B"	"C"	"D"
5	$3\frac{1}{4}"$	$0.178" \pm 0.001"$	$1\frac{1}{4}"$	$2^{\circ}52' \pm 2'$
7	$3\frac{1}{4}"$	$0.257" \pm 0.001"$	2"	$2^{\circ}52' \pm 2'$
9	1"	$0.335" \pm 0.001"$	2"	$2^{\circ}52' \pm 2'$
11	1"	$0.414" \pm 0.001"$	$2\frac{1}{8}"$	$2^{\circ}52' \pm 2'$
15	$1\frac{1}{4}"$	$0.571" \pm 0.001"$	$2\frac{3}{8}"$	$2^{\circ}52' \pm 2'$
30	2"	$1.162" \pm 0.001"$	$2\frac{5}{8}"$	$2^{\circ}52' \pm 2'$
65	$3\frac{1}{4}"$	$2.540" \pm 0.001"$	$3\frac{1}{4}"$	$2^{\circ}52' \pm 2'$

Sleeve Dimensions

"E"	"F"	"G"
$1.083" \pm 0.001"$	$1\frac{1}{4}"$	$1.815" \pm 0.002"$
$1.389" \pm 0.001"$	$2\frac{1}{8}"$	$2.003" \pm 0.002"$
$1.633" \pm 0.001"$	$3\frac{1}{4}"$	$2.003" \pm 0.002"$
$1.939" \pm 0.001"$	$4\frac{1}{8}"$	$2.190" \pm 0.002"$
$2.468" \pm 0.001"$	$5\frac{1}{8}"$	$2.315" \pm 0.002"$
$4.416" \pm 0.001"$	$11\frac{1}{4}"$	$2.628" \pm 0.002"$
$8.923" \pm 0.001"$	$25\frac{3}{4}"$	$3.254" \pm 0.002"$

STANDARD TAPER GRINDER AND SLEEVE (SHORT)

Grinder Dimensions

No.	"A"	"B"	"C"	"D"	"E"	"F"
5	$0.138" \pm 0.001"$	$2^{\circ}52' \pm 2'$	$1\frac{1}{2}"$	1"	$1\frac{1}{4}"$	$2\frac{1}{4}"$
7 & 9	$0.217" \pm 0.001"$	$2^{\circ}52' \pm 2'$	$1\frac{1}{2}"$	1"	$2\frac{3}{4}"$	$3\frac{3}{4}"$
11	$0.374" \pm 0.001"$	$2^{\circ}52' \pm 2'$	$1\frac{1}{2}"$	1"	$2\frac{1}{8}"$	$3\frac{1}{8}"$
15	$0.531" \pm 0.001"$	$2^{\circ}52' \pm 2'$	$3\frac{1}{4}"$	1"	$2\frac{1}{8}"$	$3\frac{1}{8}"$
30	$1.122" \pm 0.001"$	$2^{\circ}52' \pm 2'$	$3\frac{1}{4}"$	1"	$2\frac{5}{8}"$	$3\frac{5}{8}"$
65	$2.500" \pm 0.001"$	$2^{\circ}52' \pm 2'$	$3\frac{1}{4}"$	1"	$3\frac{1}{4}"$	$4\frac{1}{4}"$

Sleeve Dimensions

"G"	"H"	"I"
$1.027" \pm 0.001"$	$1.815" \pm 0.002"$	$1\frac{1}{4}"$
$1.561" \pm 0.001"$	$2.753" \pm 0.002"$	$2\frac{3}{8}"$
$1.895" \pm 0.001"$	$2\frac{1}{4}"$	$3\frac{1}{8}"$
$2.453" \pm 0.001"$	$2\frac{3}{8}"$	$5\frac{1}{4}"$
$4.368" \pm 0.001"$	$2\frac{1}{2}"$	$11\frac{1}{4}"$
$8.880" \pm 0.001"$	$3\frac{1}{8}"$	$25\frac{1}{8}"$

hand is closed by fusing the glass and a blowing tube with swivel is connected to the point held in the left hand. The tube is then heated over a 3" section near the point held in the right hand. The glass is allowed to accumulate by fusion under continued rotation. As the glass collapses it is blown out to the original tube diameter. Two motions are necessary in this operation: the tube must be rotated for even heating and must be moved along the horizontal to heat the 3" section. This operation of gathering the glass will require considerable practice. The tube must not be twisted and an attempt should be made to keep the wall thickness the same over the heated section. After the desired wall thickness

has been obtained, the tube is then heated over a $\frac{1}{2}$ " circular section of thickened glass end which is nearest the left hand and at the point where the thickened glass meets the original glass tube. This section is then blown out to a bulb with a diameter $\frac{1}{4}$ " greater than the original tubing. This bulb is shown in Fig. 57. The wall thickness of the bulb will be comparable to that of the original tubing because of the accumulation of glass at that point.

The open end of the joint is made next. The ground section of the joint is to be 40 mm. in length; therefore, at least

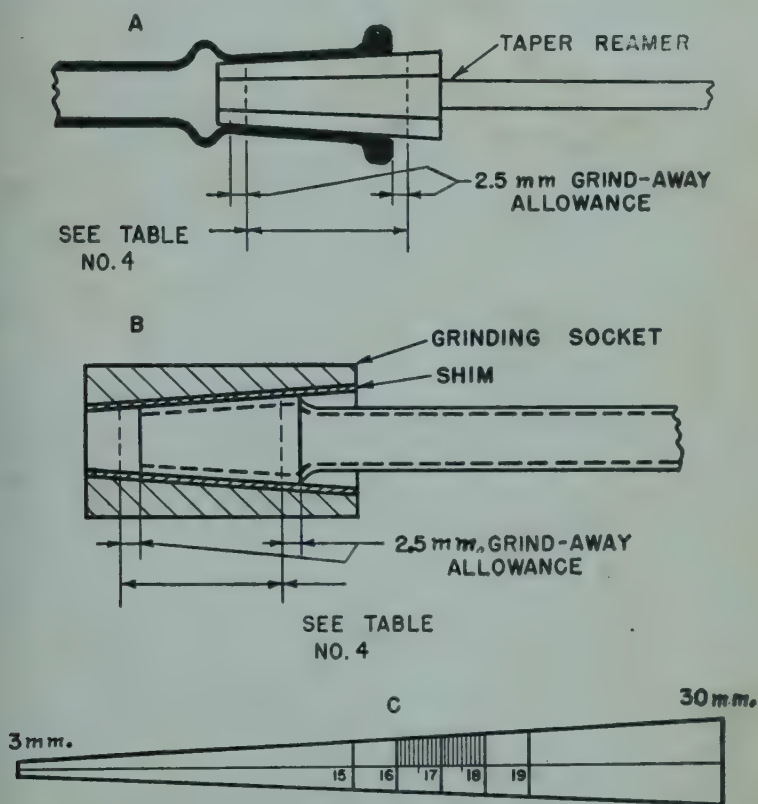


Fig. 65

44 mm. of glass from the base of the bulb to the end is required for the ground section and the round beaded end of the outer member. A chalk mark or very small file mark is made at a point 44 mm. from the base of the bulb and the glass is cut in the burner flame. The excess glass is drawn away and the tip is heated until the glass is fused back to the mark. The fused glass is blown to a thin bulb which is scraped away with forceps. At this point the reamer which is to be used must be calipered and marked. The dimensions are obtained from the taper scale. A vernier caliper is

moved along the scale until the scale cross-section measurement of 24 mm. is obtained. This is to be the finished diameter at the top of the joint. However, a certain amount of grinding must be done before this final diameter is reached, so a certain length along the scale must be allowed. A satisfactory grindaway is about 2.5 mm., so the vernier caliper is moved down the scale 2.5 mm. The diameter at this point is smaller than 24 mm. (It should be pointed out here that the 2.5 mm. is a measurement along the horizontal and not along the taper of the scale.) The diameter of the scale is obtained and the reamer is marked at this diameter. The thickened glass is then heated around the opening and, when the glass begins to sag or flow slightly, the tube is removed from the flame and the reamer is inserted and turned in the direction opposite to that in which the tube is turned. The direction is reversed after each partial turn. The reamer must not be forced or pushed too tightly into the glass. The tube is again heated but this time it is important that the section where the taper ends be heated as well as the glass that has been tapered. This process is repeated until a true taper is obtained to the base of the cone. Sometimes it is necessary to smooth out the outside of the taper. This is accomplished by heating the glass and using a flat carbon tool. The reamer must be used after each smoothing operation. The end of the taper is then heated and the thickened glass is tooled to a form as shown in Fig. 65A. After the end is completed, the taper is enlarged until the end of tube is in line with the mark on the taper, Fig. 65A. After a thorough annealing the taper is now ready for grinding and has the required grindaway allowance of 2.5 mm., Fig. 65A.

The Inner Member

The inner member is made from the same tubing used in forming the outer member. A point is pulled on both ends of the tube which is 14" in length. While the glass points are allowed to cool, three calipers should be set by using the scale as a gage. The outer member was made undersize for grindaway allowance and for a similar reason the inner member must be made oversize. The 24 mm. point on the scale is recorded and one caliper is set for a diameter 2.5 mm. toward the wider end of the scale. This point will be designated as number 1. The second caliper is set at 40 mm. The third caliper is set at the diameter of the scale 40 mm. from point 1.

The inner taper is more difficult to make because it must be shaped by hand. The glass tube is heated with rotation at a point 3" from the right tube end. Enough glass is collected for a heavy-walled shoulder.

After the shoulder is blown the glass from this shoulder to within $\frac{1}{2}$ " of the end of the tube is heated and glass is accumulated beyond the shoulder to the end. The glass is collapsed and blown out to the tube diameter on one end and the diameter of the shoulder on the other. Imperfections such as small bulges are smoothed down with a flat carbon tool. As the glass is collected, the taper is formed by pulling down the expanded section. One must be careful to do this slowly, *i.e.*, the glass accumulation must be faster than the pulling-down operation since the wall thickness is decreased by the latter operation. As the taper forms, one should caliper the diameter of the two ends, the diameters

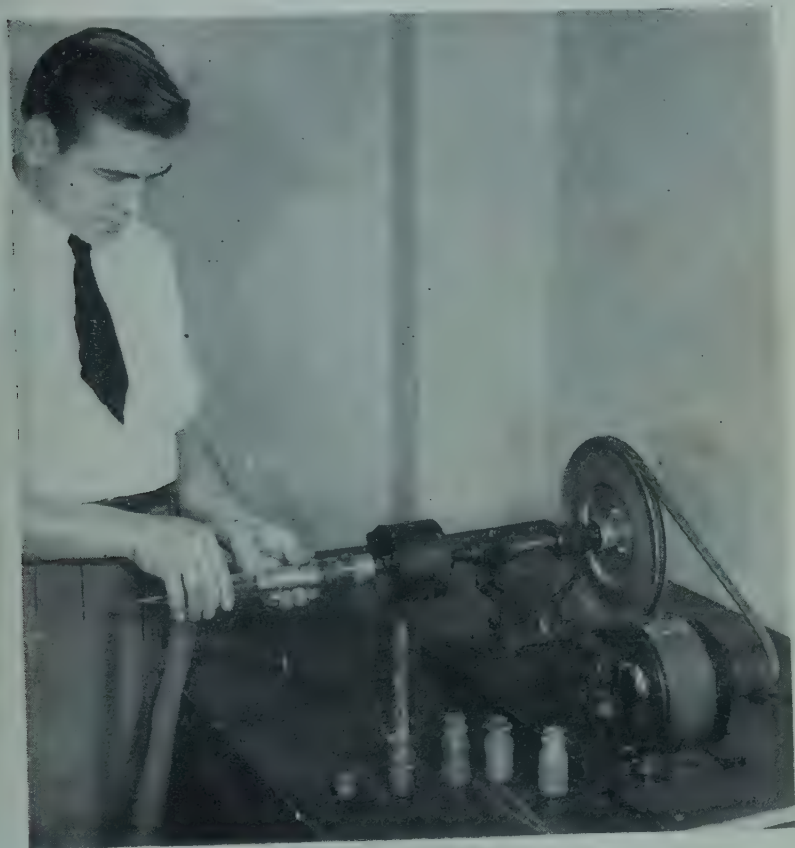


Fig. 66

at the shoulder and 40 mm. below the shoulder. After these diameters have been obtained, the taper is cut at the point 40 mm. from the shoulder either by the burner or cutting wheel. When the former method is used, the end will have to be tooled smooth with a round and a flat carbon tool. Wheel cuts should be fire polished. In production work this inner joint is also tooled.

TAPER GRINDING

(Grinding materials must be harder than glass. Various grades of carborundum or emery have been used successfully. Four grades of grinding compounds can be used for suitable grindings: These are:

1. Carborundum No. 220 is used for rough grinding.
2. Carborundum No. 320 is suitable for intermediate grinding.
3. Carborundum No. 600 is suitable for the final grinding step.
4. Turkish emery, size SF-10 is used for the final polishing.)

The grinding of the inner or outer members is best done with grinding equipment shown in Fig. 66. Here the operator is holding the outer member of a joint on the taper grinder. The unit consists of a motor whose speed is reduced to 100 r.p.m. by a pulley arrangement. The three-jaw chuck is fastened to the arbor of the pulley. The taper is centered in the chuck and the grinding sleeve is fastened to the taper with tape. A mark is made on the taper sleeve at the point where the diameter is 24 mm. Carborundum grit No. 220 is then mixed with water and applied to the joint and taper with a spatula. The motor is started and the joint is held against the grinding taper. One must be very careful that the ground surface is always wet.

As the grinding proceeds the cutting sound will diminish, indicating that another application of the carborundum grit and water mixture is needed. The ground surface should be examined before each application. Most of the cutting is done with No. 220 grit. The sleeve and joint should then be washed free of the coarse grit and the grinding is continued with carborundum No. 320 in water. This finer grit works into the soft metal sleeve and creates a planing action which begins to smooth out the marks caused by the coarser grit. When the mark in the sleeve coincides with the open end of the outer member, a new sleeve is put on the taper and the joint is thoroughly washed. Carborundum grit No. 600 in water is then used. The new sleeve will permit the production of a more accurate taper. The joint is ground until the correct diameter is obtained. It is then thoroughly washed and finished with Turkish emery SF-10.

The inner member is ground in the same way except that a grinding socket is used in the chuck. The grind-away allowance is determined as shown in Fig. 65B. The diameter of the shoulder on the joint should be measured periodically during the last stage of the grinding process. A complete joint, ground as just described will be interchangeable if made correctly. If a vacuum-tight joint is desired, it is necessary to grind the inner and outer members

together with 600 carborundum, then Turkish emery SF-10 or No. 900 mesh grit. This procedure destroys the interchangeable character of the joint.

MAKING STOPCOCKS

Stopcocks as shown in Fig. 60 are made up in two parts: the plug or inner member, and the shell or barrel which constitutes the outer member. In the fabrication of a stop-

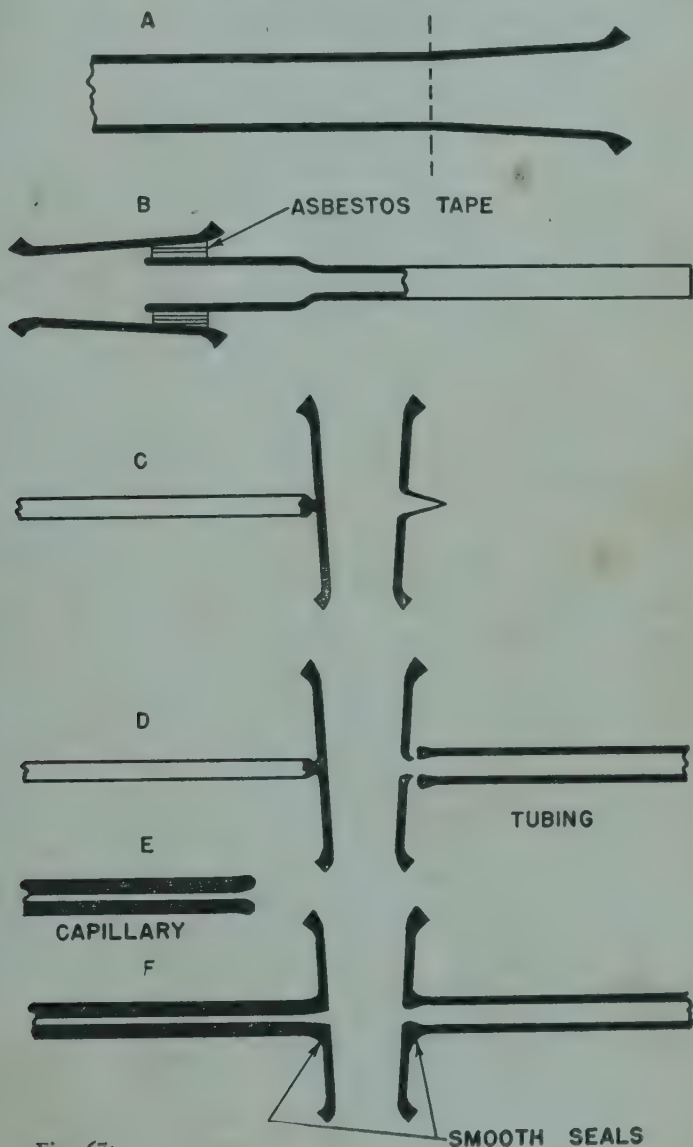


Fig. 67

cock, two glass surfaces must be shaped and ground much in the same manner as in making ground joints. There are,

however, two additional features which lead to complications if one is not careful in critical construction details. First, two inlet tubes must be sealed to the barrel and, secondly, the plug bore must be exactly aligned with the outlet tube openings. The procedure for making a stopcock is as follows:

1. The choice of tubing size for the barrel will depend upon the size of stopcock. As an example, suppose that a No. 2 standard taper stopcock is to be made. The standard dimensions of this stopcock as given in Table 6 show that the diameter of the plug at the center line of the bore is 12 mm., that the bore hole is 2 mm. in diameter and that the shell is 30 mm. long. The standard scale will be quite useful in choosing glass with a suitable tube diameter. The shell will be made undersize for grindaway. The diameter at the center line of the bore is obtained by setting a caliper at the diameter of the scale, 2.5 mm. along the scale horizontal line, from the 12 mm. diameter reading. This diameter will be smaller than 12 mm. since the 2.5 mm. distance was taken toward the point of the scale. This is the reference point from which the second point is established by measuring 15 mm. on the scale toward its base. The diameter at this point is set on a caliper which is used in setting and marking the diameter on a standard taper reamer. Measurement in the opposite direction will establish the diameter of the small end of the shell. The barrel should have a heavy wall because two outlet tubes must be sealed to it, and if the wall is thin there is more danger of deforming the tapered wall during the sealing. From the above measurement the diameter of the small end of the shell is about 10.5 mm. One must now choose glass tubing for the barrel. Any tube size from 12 to 18 mm. will be satisfactory but it is advisable to choose the latter. The diameter is worked down as the glass is gathered. Heavy-walled Pyrex combustion tubing 13 mm. O.D. is ideal in this case and is conveniently used when available. This thick-walled tubing eliminates gathering of glass. If ordinary Pyrex tubing is used, a section 12" long is taken from stock and a point is pulled on each end. The glass is then gathered and collapsed by fusing it in a cross fire. This procedure was outlined in the production of standard taper joints. The wall thickness of the glass is increased and the diameter is decreased. The glass must be kept smooth by blowing out slightly and working it down with a flat carbon tool. The glass tube is then opened by using the small burner flame.

2. The rough edge is tooled down by heating the end in the flame and using both a round and flat carbon tool. The reamer which has been marked at the desired undersize diameter is then used to form the taper. The same procedure should be used as was described under the preparation of a taper for the standard joint. After the taper is reamed to

size, it is annealed and allowed to cool. The taper is then cut at the dotted line, Fig. 67A. The taper is then mounted on a glass holder and the small end is tooled to the shape shown in Fig. 67B.

3. The center line of the bore is then marked on the tapered shell. A 3 mm. glass rod is attached by touching the end of the glass rod which is fused in the burner, to the section of the shell which was marked and fused slightly at this mark. The glass holder is then removed and a spot *directly opposite* the point where the glass rod is attached, is heated in a pin-point burner flame. The barrel is rotated by twirling the glass rod with the tips of the fingers. The glass is drawn out to a small cone by touching the fused glass with a glass rod, pulling the rod directly away from the shell, Fig. 67C. The thin cone is scraped away and the glass is fire polished to give a smooth round hole in the shell.

4. The two outlet tubes should now be prepared. If these tubes are to be of regular glass tubing, a constriction is made in the tube. The glass is cut at the center of the constriction and the end is flattened by the carbon tool. Capillary tubing must be opened by blowing a thick-walled bulb in a capillary and cutting it at the diameter with the burner. The end is also flattened with a flat carbon tool. Both tube ends should have the form shown in Fig. 67E.

5. The rod attached to the shell is taken in the left hand and the outlet tube is held in the right hand. The burner is adjusted to a pin-point flame which is directed against the shell opening and the prepared end of the outlet tube. The glass of both the barrel and tube is heated with rotation until it appears white hot and the outlet tube is *touched* to the barrel *directly* over the hole. The glass is allowed to cool slightly. The point of contact between the barrel and outlet tube is heated with rotation to a temperature which allows the glass to flow sufficiently to give a smooth seal, Fig. 67F. Under no circumstances should the contour of the taper be altered during the above operations. The glass seal is made without blowing into any part of the system and, because the shell and outlet tube have thick glass walls, no distortion of the outlet tube bore or shell taper will be experienced unless the two are pushed together or pulled apart during the operation. The second outlet tube is sealed to the shell exactly as the first. In this case the latter will serve as a handle. The entire assembly is annealed after the second outlet tube seal is completed. Two different outlet tubes of capillary and regular tubing, are illustrated in Fig. 67F to show how each should appear when finished.

6. Several different types of plugs may be made for stop-cocks. The hollow plug, solid glass plug or partly solid plugs have been used. The production of the hollow plug will be

described first. To make it, the first operation is to set the required dimensions on calipers so that the taper can be formed. The plug must be made oversize; so the diameter of the scale 2.5 mm. toward the wider end of the scale from the reference point diameter of 12 mm. is set on a caliper. Two calipers are then set for diameters 15 mm. to the right and left from the first caliper diameter setting. The plug is then started by sealing 8 mm. tubing to an 18 mm. tube, 4" in

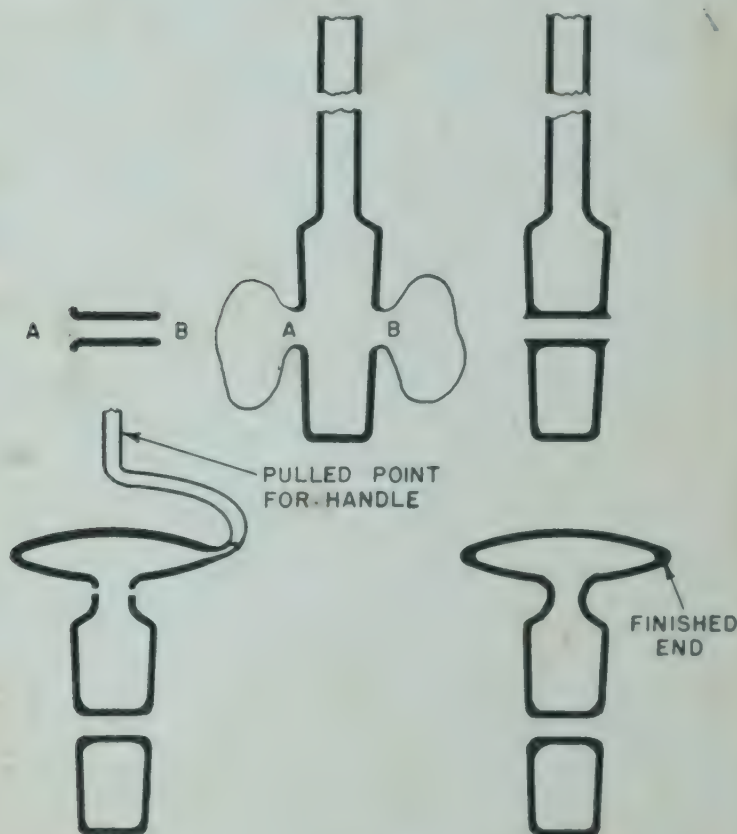


Fig. 68

length. This small tubing will serve as a point while a point is drawn on the larger tube. The taper is then made by the procedure outlined in making the taper for the inner member of the taper joint. Instead of cutting the end open, the end is closed by drawing it down sharply and removing excess glass. The end is tooled square as shown in Fig. 68. It is quite important that the three taper diameters be correct. A small tube is made as shown in Fig. 68. The internal diameter of this tube is 2 mm. The taper is then marked at the center caliper diameter and two bulbs are blown, Fig. 68. The glass of these bulbs is scraped away and the holes are fire-polished. The small tube is then inserted with ends

A and B positioned in the holes A and B of the plug. The glass of the tube and plug at A are sealed. The tube is reamed periodically to keep it open and uniform, and the glass along the taper is tooled with a flat carbon tool. The seal at B is made by heating the end of the bore tube and tooling it out against the plug. The seal is finished

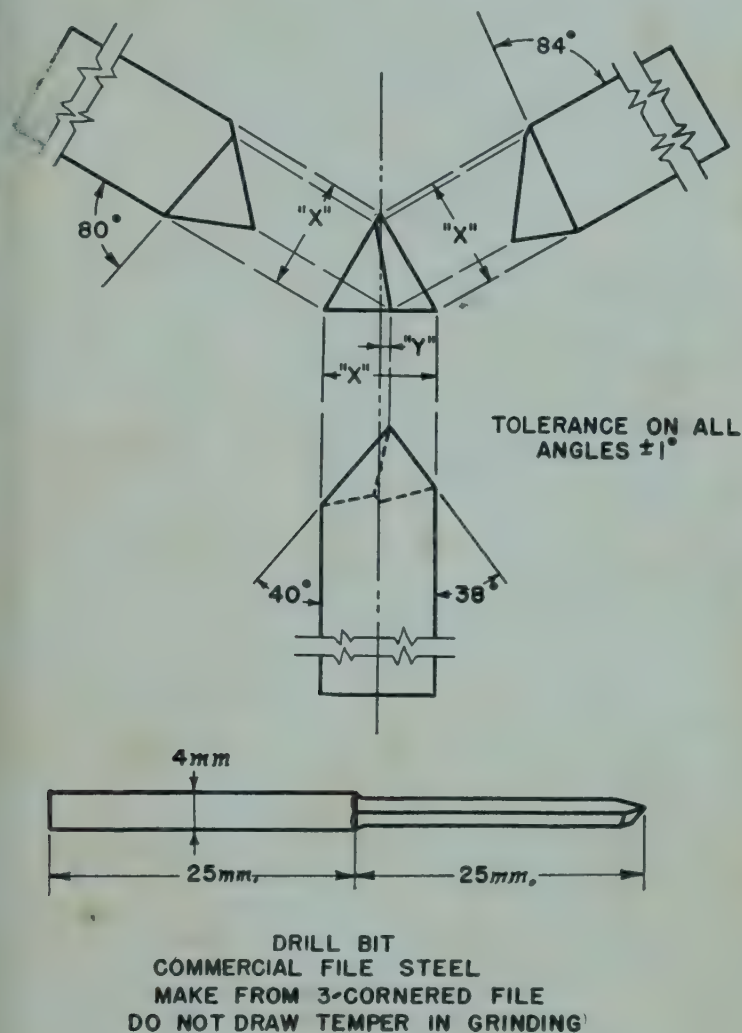


Fig. 69

exactly as seal A. The plug is then annealed. A certain amount of glass build-up is allowed as shown in Fig. 68 so that no thin spots will develop during the grinding process.

7. The barrel and plug are then ground to size with the standard grinding tools. A grindaway of 2.5 mm. is al-

lowed and one should be careful that exactly this distance of grindaway is taken, because the holes in the plug must be aligned with those of the shell.

8. The plug handle is then made as shown in Fig. 68 by side sealing the plug tubing to another tube and shaping it as shown.

The technique of shaping solid stopcock plugs is similar to the shaping of hollow plugs except that in this case solid glass rods are used and the taper is formed by drawing and tooling down the glass. Commercially, solid plugs are molded. Glass for grindaway must be allowed. The

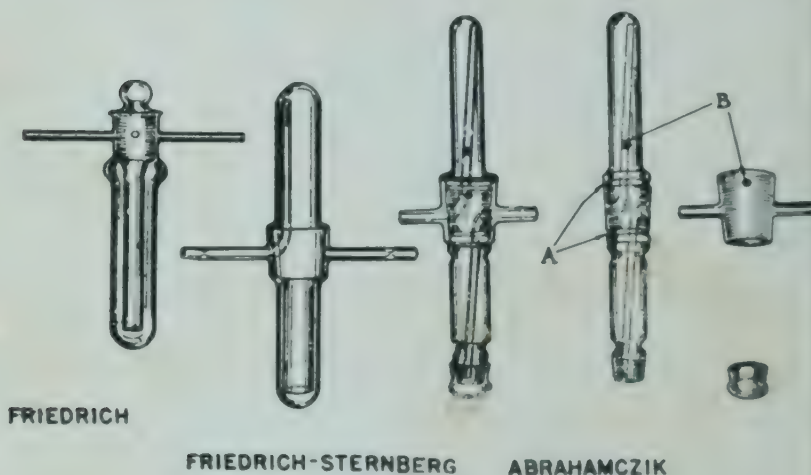


Fig. 70

bore, however, is made by drilling a hole through the glass. This technique has not been discussed. A procedure for drilling holes in glass plugs is as follows:

1. It will be assumed that the solid glass plug has been shaped to the desired taper. The position of the proposed hole is marked. The drill which is used is made from a three-cornered file and is made according to the drawing in Fig. 69. Two bore sizes are listed in the dimension log of Table 10. The drill is hardened by heating, with sub-

Size of Drill	TABLE 10	
	"X" $\pm .001$ "	"Y"
2 mm.	0.0682"	$\frac{1}{64}$ "
3 mm.	0.1023"	$\frac{1}{64}$ "

sequent quenching in mercury. The plug is placed on a vee block which has the angle of the standard taper. The hole is drilled from both sides of the plug to avoid chipping the edges of the bore. Turpentine is suitable as a lubricant in

the drilling operation. The plug is then ground in a standard taper socket by the procedure described for the hollow stopcock plug.

REGRINDING AND TESTING STOPCOCKS AND JOINTS

Standard taper stopcocks and joints are not recommended for vacuum work. The plug or inner member must be ground into the barrel or outer member in the last stage of the grinding process to make the seal required in vacuum systems. Standard ground joint and stopcocks may also be ground together, but in all cases the characteristics of interchangeability are lost. A 900-mesh grit is usually used in this work. One must be especially careful in finishing stopcocks or the outlet tube holes will partly pass the bore hole.

Several methods for testing the degree of leakage in a joint or stopcock have been used but each has shown unreliable results. A simple test is made by cleaning the ground surfaces and wetting them with water. The two members are then put together and an attempt is made to press the inner member to one side. If the seal is poor, a movement in the water contact can easily be seen.

SPECIAL DESIGN OF STOPCOCK

Numerous special designs can be given for the development of intricate stopcocks. As a specific example a micro analytical absorption tube will be described. Several absorption tubes are shown in Fig. 70.^{3, 4, 5, 6} The Abrahamczik absorption tube was modified as shown in Fig. 71.^{3, 7} Its use has been discussed by R. O. Clark and Gordon H. Stillson.⁷ The fabrication of this absorption tube is straightforward but is more difficult than the production of a standard stopcock. The glass joint is necessarily thin for low total weight. A brief description of the fabrication of this special stopcock adaption is as follows:

1. The outer member is made by reaming out a tube for a 12 mm. standard taper joint. The taper is then cut to a length of 16 mm. and two outlet tubes shaped as shown in Fig. 71 are sealed to the shell much in the same manner as the outlet tubes were sealed to the shell of the standard stopcock barrel. A spot of colored glass is fused to the shell for an indicating mark. This shell is then annealed, allowed to cool, and ground with a standard grinding tool. A small amount of grindaway is left for grinding the inner member into this outer shell. All grindaway calculations and allowances are made by using the standard taper scale.

2. The inner member is made by first drawing a standard taper to fit pre-set calipers and the large and small ends are drawn down to 8 mm. Thin-wall tubing of this

size is then sealed to each end. The taper for the joint which is to serve as the opening for charging the absorbent is then shaped. Two inner tubes are made to form with flat open ends. The ends of the tubes which are to be sealed to the inner member are shaped to contact exactly the tapered wall. These tubes are sealed to the inner member by the procedure used in starting a ring seal. They are held in place in this operation by stiff wire. Instead of blowing out the glass over the two sealed tube ends, a pointed tungsten rod 0.06" in diameter is held against the center of the seal and turned rapidly as it is heated to red heat. The force applied to the hot rod opens a smooth hole into the sealed tube. An indicator mark is fused to the

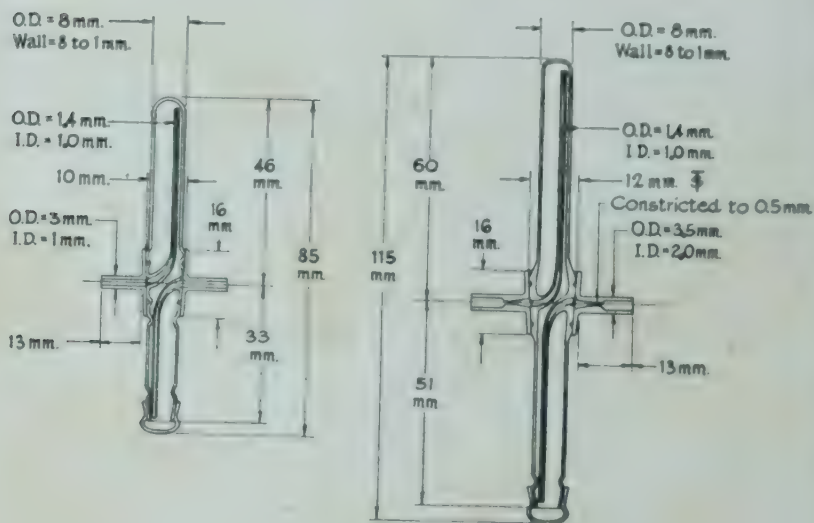


Fig. 71

tube above the joint. One end of the absorption tube is closed and the assembly is carefully annealed and ground in a short grinding socket. Two lubricant retaining rings are ground into the surface of the inner joint by using an abrasive cutting wheel and rotating both the wheel and joint to give a groove of even depth.

3. The inner and outer members are then ground together until the holes match exactly. The small cap is then made. This cap and the taper on the end of the absorption tube are ground individually and finally together to give a good seal.

Many similar examples can be given in making small or intricate joints or stopcocks, but the foregoing suffices to challenge glass workers for the development of special equipment.

CARE OF GROUND JOINTS AND STOPCOCKS

All ground joints and stopcocks should be kept clean and free of grit and dirt. Martin Shepherd has suggested that ground surfaces should receive the same care as given optical surfaces. It is certain that if ground surfaces were treated in this manner, considerable time would be saved in experimental work. Usually stopcocks and joints are neglected in the laboratory. Whenever joints and stopcocks are stored they should be thoroughly cleaned. The plug or inner member is covered with tissue paper and inserted into the outer member. One should also remember that the two outlet tubes are made of glass and that a rapid twist of the plug is dangerous. The best procedure is to use two hands, one for supporting the barrel and the other for turning the plug.

LUBRICATING STOPCOCKS AND JOINTS

All ground surfaces should be carefully lubricated. Stopcocks are best lubricated by applying the lubricant at both ends of the plug. No lubricant should be applied near the bore hole. Applicators of wood are suitable. The plug is then inserted and turned slowly in one direction until the lubricant is worked to the center. Joints are lubricated by applying lubricant along the joint length on two sides. The outer or inner joint is then turned until the lubricant is evenly distributed over the entire joint.

LUBRICANTS

Many lubricants have been used with a certain degree of success but as yet no all-purpose lubricant has been found. Some performed satisfactorily when first applied but, upon being worked by the turning of the stopcock plug, thin out and create troublesome leaks. Most lubricants cannot be used successfully over long periods of time, such as six days, especially if the stopcocks and joints are located in vacuum systems, unless one is careful in cleaning the inner member and applying the lubricant at frequent intervals.

Lubricants which are fairly satisfactory for vacuum joints and stopcocks at room temperature or for ordinary routine laboratory work are:

Apiezon—N

Celvacene, light, medium or heavy

Cello-seal

Cello-grease

Cenco-vacuseal, light and heavy body

Sisco Stopcock Grease

Distillation Products Vacuum Grease No. CB-5.

DC Stopcock Grease, high-vacuum type

Myvacene—S

The last two lubricants are special silicone greases prepared by Dow Corning Corporation. Since the characteristic of silicones is heat stability, it is quite probable that their exploitation as high temperature lubricants may be quite valuable.

Separation of Joint or Stopcock Members That Are Frozen Together

Stopcocks which have frozen plugs can be taken apart by using special plug extractors which can be purchased. The barrel is placed in a guide and a plug trigger driven by a spring removes the plug by the trigger impact. (The plugs may sometimes be removed by applying a 10% solution of

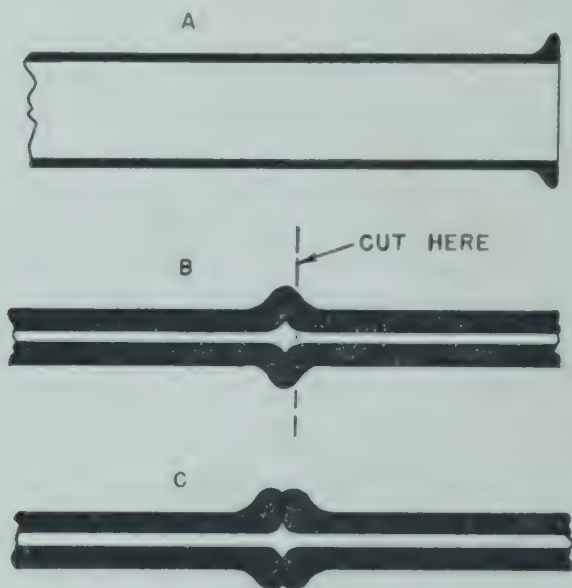


Fig. 72

Aerosol OT in ethanol. The solution containing the detergent penetrates between the ground surfaces and loosens the plug. This solution is also useful in separating the members of ground joints.)

The surest way of separating frozen members of joints or stopcocks is to apply a brush flame over the outside member. Success in this operation depends on two things. First, the flame must be hot, similar to the flame produced by the gas and air annealing burner. Second, the operation must be quickly completed: it is the more rapid heating of the outer member which loosens the joint. Delay in removing the inner member allows it to become heated. If the members do not come apart the entire stopcock or joint must be cooled before another attempt is made.

FLAT GRINDING OF GLASS FLARES AND COUPLINGS

Flat ground flares or couplings are required in glass circuits if the glass must be connected by a joint which can be closed without moving the glass system through the distance required in closing tapered or spherical joints. Two flat couplings are shown in Fig. 72, A and C. The glass for the coupling in Fig. 72A is made by collecting and working the glass at the end of the tube to a round bead and flattening this bead with a flat carbon tool. The capillary flare is made by pressing the fused glass of the capillary together while it is rotated until a heavy-walled ridge is formed. The glass is then cut slightly beyond the maximum diameter, as indicated by the dotted line in Fig. 72B. This procedure is repeated for the second flat of the coupling.

The flared ends of the glass are ground with the respective grinding compounds used in finishing stopcocks and joints. A flat glass grinding surface is used. A suitable flat grinder, built much in the same manner as a metallographic polisher, is very useful for flat grinding. A glass disk is mounted on the turntable. The grinding compound is put upon the disk with sufficient water to wet the entire surface. The glass is pressed against the rotating disk. In order to avoid breaking the tube when the flare is being ground, the grip should be low, near the flare. The flare is moved from the center to the outer edge of the disk on the side where the latter is moving away from the operator. The flare is rotated during grinding. The entire surface is carefully cleaned with water before the next grinding powder is used.

The finished couplings are lubricated and clamps similar in design to those used for spherical joints can be used for holding the two members together. The efficiency of these couplings is dependent upon the cross-sectional diameter and the accuracy with which the two members are ground. Sometimes it is necessary to grind the two together in the final grinding stage, but this can be accomplished only if a guide is made to hold the two tubes in an exact perpendicular position. The flat flare shown in Fig. 72A can be used in making optical glass cells. The optical glass is sealed to each flared end by using suitable sealing cement.

GROUND GLASS CHECK VALVES

Check valves are used in glass systems for the intermittent flow of gases or liquids. They are sometimes installed to prevent certain liquids from escaping into other parts of a closed system. Liquid or gas pumps also are fitted with suitable check valves.

Three of the more common and reliable types of check valves have been chosen for discussion. The check valves shown in Fig. 73 are incorporated in automatic Toepler

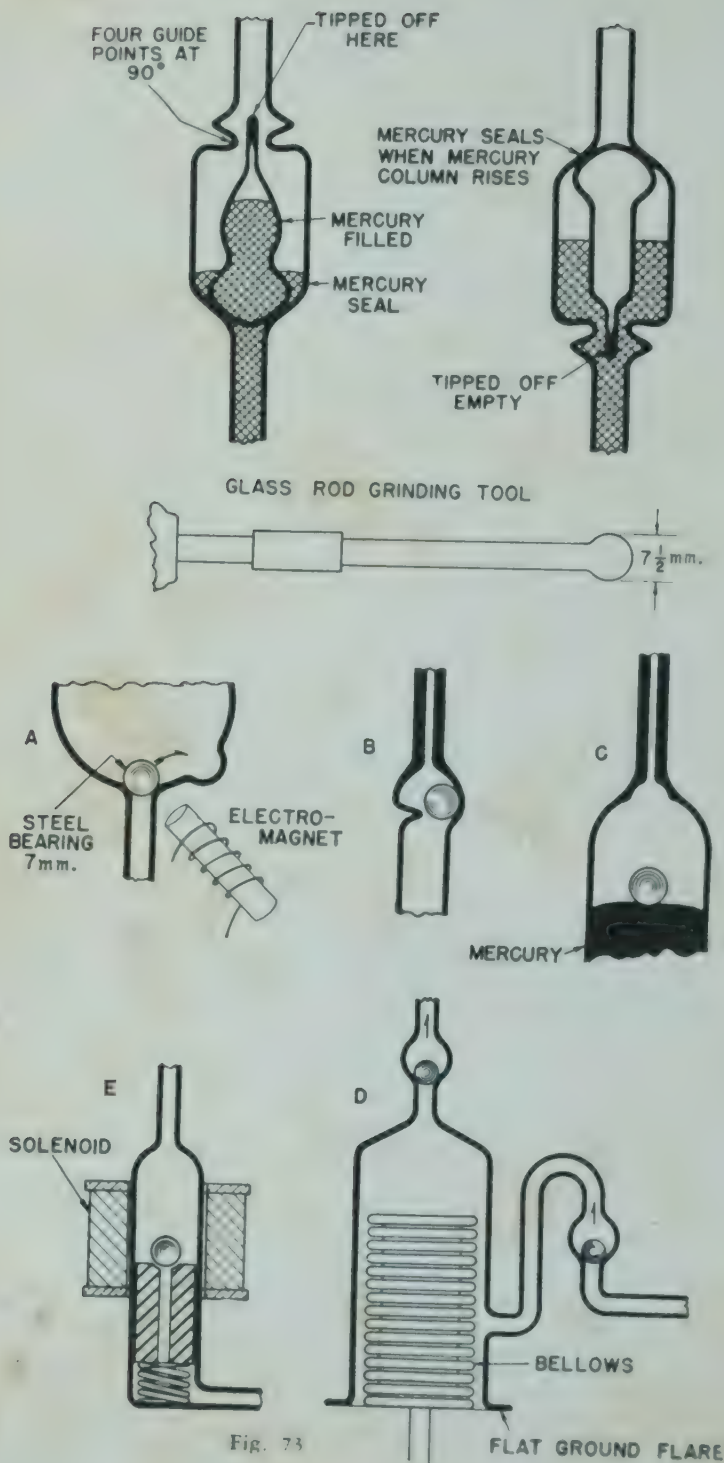


Fig. 73

pumps which are used in transferring gases. The procedure in making the valves is quite simple. Two floats are made as shown in Fig. 73. The extension tubes which are open serve as handles for grinding the float against the body. The floats are ground into the body to form a check seat. One is nearly filled with mercury and tipped off. The second is left empty because it must operate as a float. The floats are then sealed into the body by making the second reduced seal. Four glass indentations are made to center the check. These indentations are made by heating a spot on the shoulder of the body and pushing the glass toward the check with the point of a three-cornered file. Toepler pumps normally use mercury as a confining liquid and this helps in forming a seal, either by getting above the check and forming a seal with the check seat, or, forcing the empty float of the second valve against the ground seat. It should be noted that the ground seat is a combination of a taper on the body, and a sphere on the float.

Ball check valves with metal or ground glass balls are shown in Fig. 73. A metal ball is used for the check ball in Fig. 73A. The body of the check is made by joining a small tube to a larger tube. A small indentation on the shoulder serves as a holder for the check ball which is moved with an electromagnet. The check seat is ground with the glass rod grinding tool made in the form shown in Fig. 73. This rod is made by fusing the end of a glass rod until a solid glass sphere is obtained with a diameter of 7.5 mm. This rod is wrapped with Scotch tape and then mounted in the grinding chuck. The four respective grinding compounds are used in the grinding process. The glass sphere of the tool is ground to a taper as the grinding proceeds. This is advantageous because the ball will seat better against a taper than against a curved surface.

The check valves shown in Fig. 73B and C are used extensively in gas analysis apparatus. The check in Fig. 73B is made by sealing a tube to capillary tube and forming a small bulb at the seal. The former is cut about $\frac{1}{2}$ " from the seal. The check seat is ground into the capillary. In order to confine the ball in the bulb with as small a dead space as possible, it is advisable to hold the former to the seat by connecting a vacuum line to the capillary. The tubing is then sealed to the bulb and an indentation is made with the end of a file. This indentation keeps the ball from forming a partial seal at the other outlet of the bulb. The arrangement of two simple ball checks sealed into bulbs is shown in Fig. 73D. These checks serve as the inlet and outlet checks for a small sylphon bellows displacement pump.

Another pump arrangement is shown in Fig. 73E. The metal plunger is activated by a solenoid. The ball operates as a check by sealing on the upward stroke and releasing on the downward stroke.

In some of the check valves described thus far, glass balls have been recommended. These can be purchased from Fisher Scientific Company. The diameter of the ground-surface glass balls is 7 mm. If special sizes are needed, glass balls can be made by gathering glass on the end of a rod to the correct size. This ball is then cut by sticking a small rod

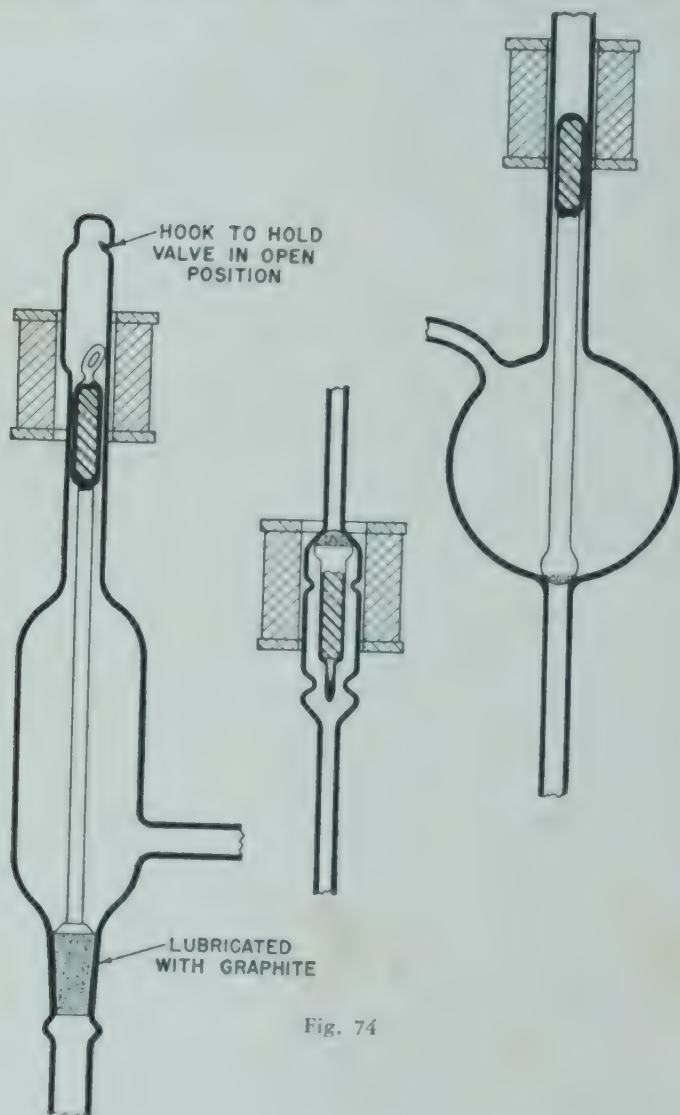


Fig. 74

to the glass and cutting the original rod from the ball. If the glass is not flowed too much, the attached rod can be broken away. The ball surfaces are ground by placing several balls between two glass plates, one of which is wetted with grinding compound. The top plate is then pressed against the balls and pushed in a circular motion.

The operation of glass valves or checks by an electromagnet has offered a satisfactory means of controlling glass and liquid flow. Valves of this type are shown in Fig. 74. The soft iron core is enclosed in glass. The glass is prepared to fit over the iron core which is then heated until the iron turns blue. It is then immediately dropped into the glass and the latter is sealed. The fabrication of the valves is straightforward and need not be discussed.

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CHAPTER VIII.

GLASS-TO-METAL SEALS

The production of vacuum-tight seals for incandescent lamps and x-ray tubes was one of the earliest important laboratory applications of glass-to-metal seals. With the commercialization of electricity and the universal use of lamps, tubes and other electrical devices, durable seals were not only highly developed but industrialized. Considerable advances in sealing glass to metal resulted from extensive research in compounding specific glasses and metal alloys. In this connection the glass blower has been indispensable as an aid to the development engineer. Techniques in making glass-to-metal seals were developed as each metal alloy and glass was tested, and through this knowledge of handling the special metals and alloys, production machine seals have become a reality.

Platinum was among the first metals used in making glass-to-metal seals because of its resistance to oxidation and the availability of glass at that time, which yielded good seals with it. Edison's incandescent lamp in 1879 and the x-ray tubes which were produced in the United States in 1895¹ were made with platinum leads through the glass. Platinum, however, was gradually replaced by other metals and alloys for economic reasons. Although it is not used in making large-volume commercial products, platinum does have some special applications for glass-to-metal seals for laboratory uses.

A successful substitute for platinum was patented by B. E. Eldred in 1913.² This wire, called Dumet, consists of a copper-coated nickel steel alloy containing 38% nickel. The wire is made by fusing or welding a layer of copper, 0.054" thick, to a round nickel alloy billet with a diameter of 0.892". This billet is then drawn to a wire with a diameter of 0.008 to 0.015". The thickness of the copper is about 0.00005". This wire is still used in lamp and vacuum tube manufacture.

Manufacturers of industrial tubes adopted tungsten³ as a metal for glass-to-metal seals in 1915. This metal was successful for seals with hard glasses which were stable to thermal shock. Molybdenum⁴ was also used but with this metal special glasses were required for sealing purposes. The sealing of molybdenum to glass also required a special sealing technique because of its rapid oxidizing characteristics. Seals with both tungsten and molybdenum are still used and on occasions are quite useful in making equipment for the research laboratory.

Glass-to-copper seals were developed by W. G. Housekeeper⁴ in 1923. Although copper has a different coefficient of expansion from that of glasses which have been successfully used with it, special procedures have been developed for making glass-to-copper seals. Four different types of seals were investigated:

1. Glass-to-copper seal for electrical conductors into tubes were prepared by using flattened copper wire.
2. Thin copper ribbon was sealed into glass.
3. Copper disks were sealed to glass.
4. Glass tubes were sealed to copper tubes.

A study of the iron-nickel-cobalt alloys by Howard Scott^{5,6} in 1930 brought about the development of the alloy Kovar. This alloy is unique because its temperature coefficient of expansion is nearly the same as that of some glasses with which it is used for making glass-to-metal seals. Other alloys of this system were developed, as well as alloys of the chromium series. Glass-to-metal seals of these alloys were responsible for the metal radio tube which supplanted, to a certain extent, the all-glass envelope tube. The metal tube, however, is dependent upon glass-to-metal seals for insulation and vacuum-tight characteristics.

FUNDAMENTAL PRINCIPLES INVOLVED IN GLASS-TO-METAL SEALS

Certain properties of the glass and metal must be known before good glass-to-metal seals can be made. The glass and metal must fulfill two primary requirements before successful seals can be realized:

1. The glass must wet the surface of the metal.
2. The stresses which are set up in the glass by thermal expansion and contraction must not exceed the tensile strength of the glass.

The first requirement may be confusing. It has been shown that the glass actually dissolves in the oxide layer which covers the metal. Hull and Burger⁷ have shown that when a glass bead is placed on a metal plate which is free of oxide and both are placed in a furnace with a hydrogen atmosphere, no seal is obtained. Similar negative results were obtained with an atmosphere of an inert gas such as pure nitrogen or carbon dioxide. But when the metal is oxidized and placed into the furnace with the glass bead in an inert atmosphere, the glass forms a strong seal on the metal. It is thus important that the metal be oxidized before a seal with glass is attempted. The degree of oxidation is *very* important. If the oxide layer is too thin, the glass cannot form a strong bond with the metal and a good durable seal is not obtained. If the oxide layer is too thick, the glass cannot dissolve to the required depth in the layer and poor seals

result. The success in covering the metal with a suitable oxide film is best attained by experience. Most metals and alloys are oxidized sufficiently by heating in the burner as the seal is made. Some, however, require special techniques in oxidizing the surface.

A properly annealed glass-to-metal seal will be free of strains if the glass and metal have the same coefficient of expansion over the whole temperature range—from the annealing temperature of the glass to room temperature. Unfortunately, the physical characteristics of metals and glasses over this temperature range are different. The coefficient of expansion of metals is nearly linear, while the expansion of all glasses passes through a transition point and increases more rapidly beyond temperatures of 50 to 100°C. below the lowest practical annealing temperature. These characteristics are shown in Fig. 75.⁷ The curves of the three metals have higher coefficients of expansion than any practical standard glass. Pyrex glass, on the other hand, has a lower coefficient of expansion than any of the metals or alloys. The curves of some of the standard glasses show a transition as the softening point is approached. This change in expansion is not matched by any of the metals and the best that can be done is to match the glass and metal

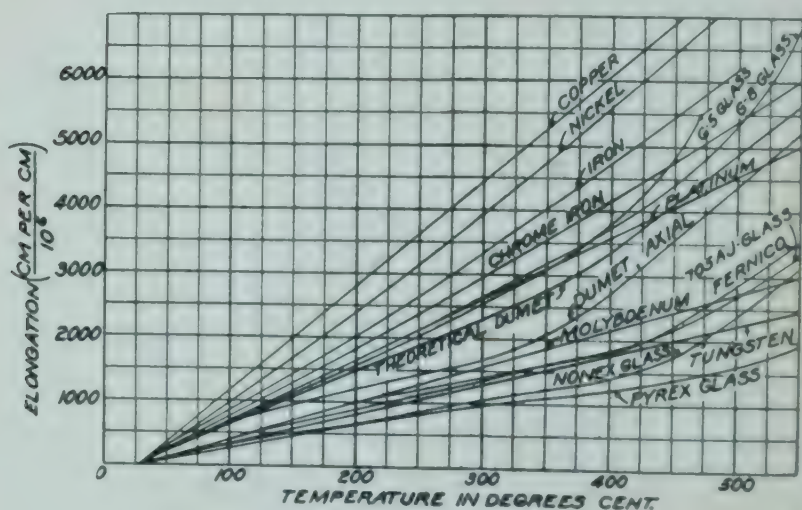


Fig. 75

curves at the annealing point and at room temperature. As an example, chrome, iron and G-8 glass have equal expansions at about 508°C. and at room temperature. A successful glass-to-metal seal could be made with this glass and alloy. Special attention should be called to the curve of the alloy Fernico.⁷ It will be noted that the curve of the 705AJ glass nearly matches that of Fernico. This glass is used for

sealing to Fernico or the similar alloy Kovar. Fernico is an alloy containing 54% iron, 28% nickel and 18% cobalt. Kovar contains 53.7% iron, 29% nickel, 17% cobalt and 0.3% manganese.

The physical properties of a number of glasses are given in Table 11. The Corning Glass Works code and laboratory numbers for each glass are given and the respective metal or alloy recommended for each is listed. Pyrex glass Number 774 is in the table but no metal is recommended for seals. This is borne out by the expansion curve of Pyrex in Fig. 75. Since most laboratory equipment is made of Pyrex, it is necessary to use a graded seal between the glass sealed to the metal and Pyrex. A sealing glass series for the graded seal is given in Table 3. Recommended European glasses for various metals are given in Table 12.⁸

TABLE 11
PHYSICAL PROPERTIES OF GLASS

Corning Glass Code	Lab.	Temperature	Softening Point, °C.	Annealing Point °C.	Strain Point °C.	Sealing Metal
		Coefficient of Expansion ×10 ⁷				
001	G1	91	626	428	397	Sylvania #4 Driver Harris #14 Platinum
008	G8	92	696	510	475	Sylvania #4 Platinum
011	G164HC	128	612	448	423	Iron SAE-1010
012	G12	89	630	433	400	Platinum Sylvania #4
024	G125BB	96	607	425	397	Sealmet #28 Driver Harris
778	GT70	37	763	498	464	Tungsten
3320	G371BN	40	784	535	497	Tungsten
704	G705BA	47	697	484	450	Kovar & Fernico
7052	G705FN	47	708	430	442	Kovar & Fernico Molybdenum
706	G705AO	50	690	495	463	Molybdenum Kovar & Fernico
752	G750AJ	61	747	566	530	Kovar & Fernico Does not match molybdenum
753	G805F	71	728	557	528	No metal to match
755	G805G	79	716	546	516	No metal to match
756	G705A1	86	702	536	503	Platinum
772	G702P	36	755	518	484	Tungsten
775	G705R	41	704	467	431	Tungsten
8160	814KW	91	627	433	399	Sylvania #4 Driver Harris #14 Platinum
774	726MX	32-33	819	553	510	
Fused Quartz		5.8	-	1120	1020	

The metal or alloy must be gas-free before good glass-to-metal seals can be obtained. Some metals require no preliminary degassing because they are freed from gas during

TABLE 12

INDUSTRIAL METALS FOR VACUUM TIGHT GLASS TO METAL SEALS

Metal	Commercial Form	Coefficient of Expansion $\times 10^7$	Thermal Con. ductivity cal./ (cm.) (sec.) (deg.C.)	Resistivity ohms/mm. ² /m.	SEALING GLASS
Platinum	Technical to Pure				
	Round wire to 1.5 mm. Ring to about 50 mm. Wall thickness 0.1 to 0.15 mm.	90.2 (25-100°C.)	0.167	0.168	M-glass (Osram) 301b (Osram) Apparatus glass 301b (Osram) ¹ PT-glass 1611 (Schott) PT-glass GeGe Eff (Fischer) PT-glass (Gundelach) Apparatus glass (Gundelach) Moosbrunner glass ² G1, G5 Glass (Corning)
Ferro Nickel Vacuum fused	Round wire to 5 mm. Rings and caps to 30 mm.	89	0.038	0.45	
(a) Ni 47.5% Fe 50% Cr 1% Mn 1%					
(b) Sintered ("Ommet") Ni 48% Fe 52% Co 0.01%					
48% Fe 52% Co 0.15%	Round wire to 5 mm.	90	0.038	0.45	
Platinum Covered Wire (Core: Ni 48% Fe 51% Platinum covering 30 to 40% of total wt.)	Round wire to 3 mm.	90	-	-	
Copper Covered Wire (Core: Ni 42% Fe 58% Copper covering: 20 to 30% of total wt.)	Round wire 0.2 to 0.8 mm. put on with borax	Radial 80-100	0.4	0.04 0.06	As above M-Glass (Osram) best
Chrome Iron Cr 25-30%	Wire 2-3 mm. rods 5-12 mm. disks and rings 0.2-1.0 mm. in wall thickness	95-100 (20-100°C.)	0.05	0.5	GeGe 28 (Fischer) ⁴ Apparatus glass (Gundelach) G1, G5, G6 and G8 Glass (Corning)

Wall thickness about
1 mm.

Apparatus glass (Gundelach)

Fernichrom (Fe 37% Ni 30% Co 25% Cr 8%)	Wire, rings	92	-	-	G5 Glass (Corning) Lead glasses
Wonico (W 80% Ni 13% Co 5%)	Wire	55	-	0.13	Sodium glass V 612e (Osram)
Tungsten	Wire and rods	40-45 (20-100°C.)	0.38	0.06	V 362A (Osram) V 619i (Osram) Uranium, ⁴ Nonex ⁸ (Corning) Duranglass (Schott)
Molybdenum	Rods to 5 mm. and over	53-55 (25-100°)	0.35	0.06	1447 III, Uvioglass (Schott) V637B, V195c (Osram) G 71 or G 705 AO (Corning)
Kovar, Fernico (Ni 28-29% Co 17-18% C<0.1 Mn 0.2 Balance Fe)	Wire and Rods to 16 mm. Kings 4-30 mm. wall thickness 0.3 to 3 mm.	47 (25-450°C.) 56 (25-500°C.)	0.09	0.27	V 756 (Osram) Clear sealing G 705 AG (Corning) ⁵ Special glass 1846 G 71, G 705AO (Corning)
Copper Vacuum fused with 1-2% Mn or Electrolytic Copper	Feather edge rings and caps 15-120 mm. Wall thickness at fu- sion point 0.2-0.1 mm.	165 (0-100)	0.92	0.017	Apparatus glass (Gundelach) Pt glass (Fischer) Blue cobalt glass KHE (Gundelach), G1, G8, G71 Pyrex Glass (Corning)
Chrom Nickel Cr 21% Ni 76.5% Fe 2.3	Feather edge rings and caps; wall thick- ness at cap edge 0.05 mm.	145	0.03	1.09	Apparatus glass (Gundelach) Pt glass (Fischer) Blue cobalt glass KHE (Gundelach) G1, G8, G71 Pyrex Glass (Corning)

1. Composition: SiO₂ 68.5% Al₂O₃ 3.2% CaO 7.1 Na₂O 14.2% K₂O 6.3
2. Composition: SiO₂ 70.5% BaO 2.5% CaO 5.5 Na₂O 16.6 K₂O 1.0 Mg 3.9%
3. Composition: SiO₂ 73% B₂O₃ 16.5% PbO 6.0% Na₂O and K₂O 4.5
4. Composition: SiO₂ 76.1 B₂O₃ 16.0% Al₂O₃ 1.75 CaO 0.2% Na₂O 5.4% K₂O 0.6%
5. Composition: SiO₂ 67% B₂O₃ 22.0% Al₂O₃ 2.0 K₂O and Na₂O 6.5%
6. Composition: SiO₂ 65% B₂O₃ 23.0% Na₂O 7% Al₂O₃ 5%

the heating period just prior to sealing. Small amounts of carbon in alloys as Kovar must be removed and these alloys are conveniently degassed by heating them in a furnace at 1050°C. for 20 minutes and in a stream of hydrogen which bubbles through a water trap before it enters the furnace. The furnace is fitted with a cooling section which is used to cool the metal to 300°C. in a hydrogen stream to prevent oxidation when it is taken from the furnace.

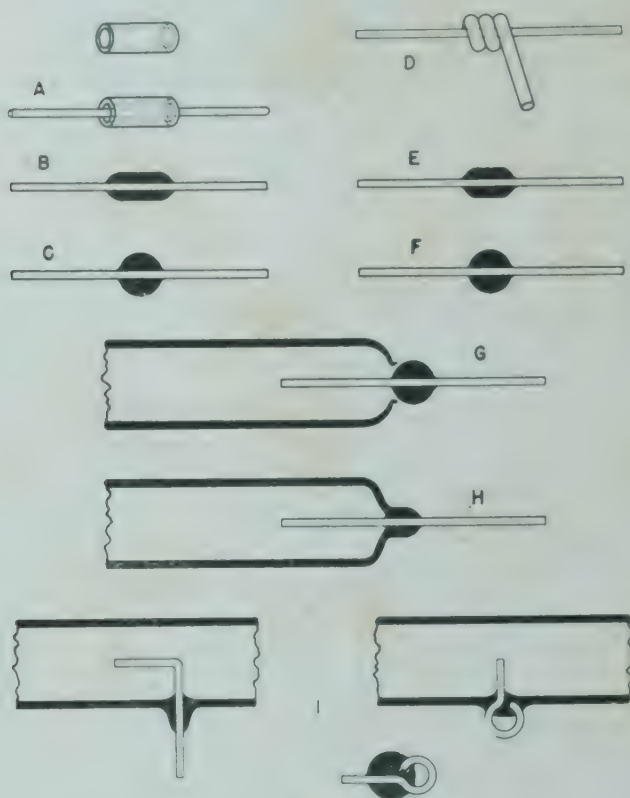


Fig. 76

In the discussion thus far, an attempt has been made to introduce a few of the fundamental principles in making glass-to-metal seals. Specific examples were cited to explain and describe some of these principles. The individual metals and alloys will be taken up in detail and the techniques in making suitable seals will be described.

PLATINUM

Platinum has an approximate linear temperature coefficient of 9×10^{-6} per degree Centigrade; and when used in making glass-to-metal seals, a glass should be chosen with

approximately this expansion. Inspection of Table 11 will show that glass with Corning glass codes of 001, 008, 012, 756 and 8160 can be used in making seals with platinum. It was generally believed that glass-to-platinum seals were successful because this metal did not oxidize, but it has been proved that platinum has an exceptionally thin stable layer of oxide.

Platinum is usually used in wire form when it is sealed to glass. The wire must first be beaded with a suitable glass. This is done in one of two ways:

1. The simpler method is illustrated in Fig. 76. The wire is clamped in a pin vise which has an asbestos handle. A small glass sleeve of about 2 mm. I.D. and 10 mm. long is then formed by fusing a 7-mm. tube, allowing it to collapse to thicken the wall and then drawing it out. The suitable size is then cut from this drawn tube. The small section is then slipped over the wire, Fig. 76A. The glass is fused at one end and after a good seal is obtained around the circumference of the wire at this end, the glass is then progressively fused toward the other end. One must be careful that no air pockets are trapped in the seal. The elongated bead (Fig. 76B) is then heated until it is fused. Surface tension of the fused glass will cause it to flow until a round bead is formed, Fig. 76C. The wire with the spherical bead is then ready to be sealed into the glass tube. The bead should not be over 4 mm. in diameter. The temperature of the bead is maintained by placing it on the screen of the Argand burner. This allows time for preparing an opening in the glass tube without the risk of cracking the bead by cooling and reheating it for the final seal.

2. The second procedure in making a bead on a wire is to fuse one end of a thin glass rod to the wire, Fig. 76D. The rod is heated until soft and wound around the wire until sufficient glass is accumulated. The rod is then cut with the flame. The coil is fused by starting at one end by heating the glass while the wire is turned slowly, Fig. 76E. Again one should be careful not to trap any air bubbles in the glass during the fusing process. It is then fused together until the glass forms a round bead, Fig. 76F.

If the wire and bead are to be sealed into the end of a tube, an end is prepared as previously described and an opening is made by blowing out a small circular portion of glass which is fused by holding the very tip of the closed tube in the flame while the tube is rotated, Fig. 76G. The hole should be slightly smaller than the bead. The hot bead and wire are then held over the hole and the former is sealed to the tube, Fig. 76H. The procedure in making side seals in tubing is the same as given above. Two such types are illustrated in Fig. 76I.

TABLE 13
PROPERTIES OF GLASSES

Corning Glass	Composition											Softening Point °C.	Temperature Coefficient of Expansion × 10 ⁻⁶				
	SiO ₂	As ₂ O ₃	PbO	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	B ₂ O ₃	TiO ₂			ZrO ₂	Sb ₂ O ₃	MnO	Mn ₂ O ₄
Pyrex	80.5			2.2				3.8	0.4	12.9						815	3.2
G-702-P	73.76	.46	5.75	1.03	.11	.07	.12			18.70						760	3.6
G-705-H	66.40		2.10	1.85	.21	.22	.79	3.49	.61	24.02	.07	.10				776	3.6
G-720-BE	80.03	.03	.10	2.28	.04	Nil	.09	2.62	1.44	12.90	.10	.10	.09	.02		810	3.1
G-707-DG	70.55	.38	Trace	1.07	.03	.07	.20	2.07	.41	25.22						800	2.8
G-702-EJ	80.00		.1	1.00				4.4		14.00						735	3.1
G-80	72.40		1.75	5.10		.25	.08	9.75	.40	10.20	.06					655	6.4-6.2
G-81																	8.5
G-70	69.07	.07	2.05	.70	.10	Nil	.50	3.87	.23	23.35	.04	.10	.11	.01		753	3.6
G-71	67.00		.05	1.17	.27	.25	.28	6.42	.47	19.00	.06		4.80	Trace			4.8
G-1	63.10		20.22	.28		.94		7.60	5.54				.88			620	9.2
G-5	61.62		22.65	.35	.15	.15		12.79	.90				.15			620	8.9
G-6	69.66		Trace	1.22		5.06		18.29	.27				4.63			675	9.8
G-705-AJ	67.3	.14	0.00	1.73	.11	0.00	.20	4.56	.94	24.6			.08	.01		758	4.5
G-8																696	9.5
G-12																627	8.8
G-9709																804	3.8

The complete area of the seal must be carefully annealed. This annealing procedure requires a careful technique as well as judgment on the part of the worker, as it is not only necessary to heat the seal uniformly, but to avoid undue softening, otherwise the glass bead and wire will sag under its own weight.

The composition of 001 or G-1 in Table 13⁹ shows that this glass contains 20.22% lead oxide (PbO). Extreme care should be exercised in the adjustment of the air-gas flame required for working the glass. The flame should be as near neutral as possible, since a reducing flame will blacken the glass and an oxidizing flame will turn the glass surface gray.

Pyrex-to-platinum seals can be made by the procedure outlined by Housekeeper for making glass-to-metal seals. Platinum electrodes can be sealed into Pyrex and successful seals can be obtained if a platinum wire 0.010" in diameter is flattened very thin (0.005") and the edges are filed to a v-shape. The thin strip is beaded as previously described except that the glass should be pressed against the platinum strip with a forceps to insure good contact with the metal. The beaded metal strip is then sealed into the desired assembly and the entire section is annealed. It was pointed out in the introductory remarks of this chapter that the glass is stressed in such a seal, but the stress is not large enough to break the glass because a very small metal strip is used.

It may be to some advantage to use a Pyrex-to-platinum seal in which mercury is used over the seal to assure a vacuum-tight seal. The seal is shown in Fig. 77A on the side of a bulb (which is part of a manostat). A platinum wire 0.01" in diameter is used. A Pyrex tube, 5 mm. in diameter and 4" in length is constricted to about the diameter of the platinum wire by fusing the glass as it is rotated in the flame, Fig. 77B. The constricted section should be about a half-inch in length. The wire is slipped into place and should be long enough to extend about a quarter of an inch beyond each end of the constriction. The Pyrex is then fused to the wire by the procedure outlined for coating wire with glass. One end of the tube is then sealed to the manostat bulb. The tube is then bent upward to the position shown in Fig. 77. The bulb and glass-to-metal seal are then carefully annealed.

The tube above the platinum seal is partly filled with mercury which serves as a conductor between the platinum and a lead wire that is put into the mercury. This eliminates the danger of breaking the wire at the glass-to-metal seal because the two are not directly connected. Any small leaks that might develop because of contraction of the wire are sealed by the mercury in the tube.

TUNGSTEN

Tungsten has a linear temperature coefficient of expansion of 4.8×10^{-6} per degree C.; and the glasses in Table 11 recommended for glass-to-tungsten seals are Corning glasses with code numbers of 778, 3320, 772 and 775. Tungsten wire is often fibrous, having longitudinal channels which may leak if sealed in vacuum tubes. Tungsten has a resistivity of 5.48 microhms (cm.²)/(cm.) at 20°C.; and to decrease the resistance of electrodes of this metal, braided copper is

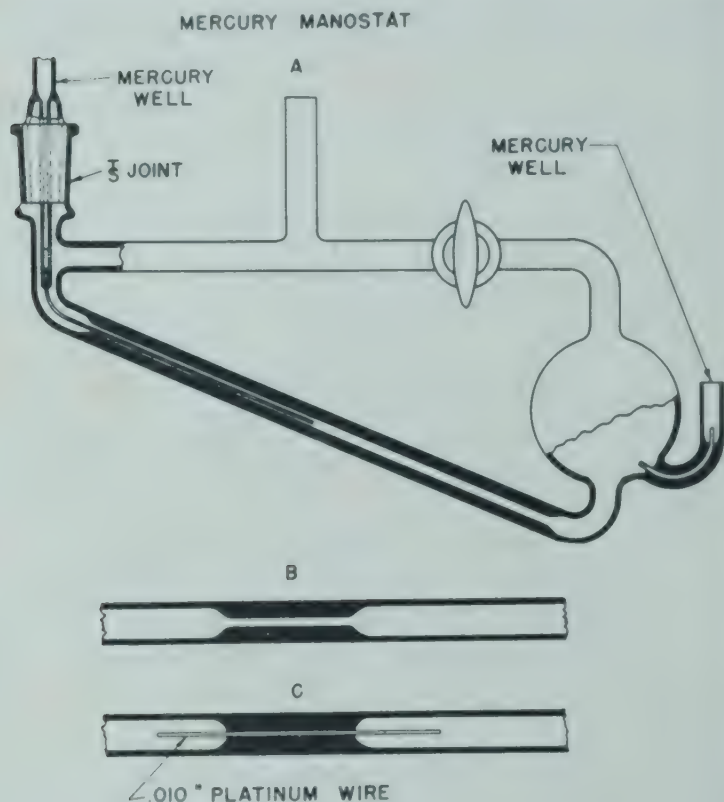


Fig. 77

butt welded to one end of the tungsten wire while a thin nickel rod is welded to the other. The butt welds, if carefully made, close the channels at both ends, thus eliminating leaks. These leads are called press welds.

When tungsten is sealed into any of the above-mentioned glasses, a glass-to-metal seal is obtained which is equal to, if not superior to, that obtained between lead glass 001 and platinum. These glasses require a higher temperature for making the seal and consequently there is danger of over-oxidizing the tungsten wire. For this reason a different technique is required when bead or press seals are made.

The following procedure is recommended regardless of the choice of the recommended glasses:

1. The wire is first degassed by heating it to white heat in an oxygen-gas flame. This is done to prevent bubbles from appearing between the wire and glass as the seal is made.

2. The wire is then heated and cleaned by rubbing it against a lump of potassium or sodium nitrite.

3. The wire is then thoroughly washed and examined. Any dark portions of oxide on the wire must be removed by repeating the second step.

4. A four-inch length of tubing of the sealing glass, 8 to 15 mm. in diameter, is then drawn down to a thin-wall tube with a diameter approximately equal to that of the tungsten

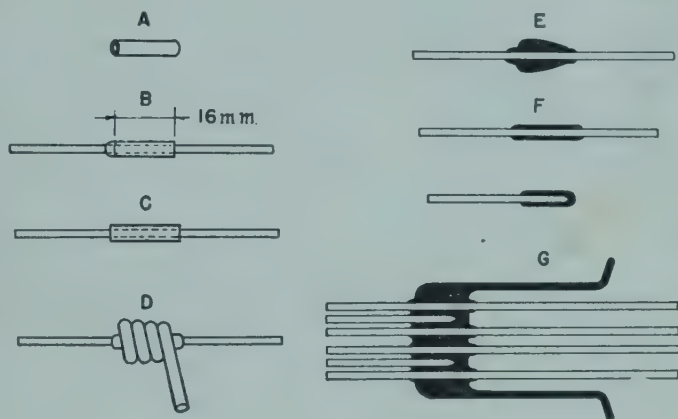


Fig. 78

wire. A section of the glass tubing which fits snugly over the wire is then cut to a length of 16 mm., Fig. 78A.

5. The clean tungsten wire is then oxidized by heating it to a *dull red heat*. This oxidizing treatment is the most important step in the entire sealing operation, and can be mastered only by individual practice. If the wire is left in the flame too long it is over-oxidized and a black seal is obtained which is not vacuum tight. If the wire is not oxidized sufficiently, the glass will not have the opportunity to dissolve in the oxide layer and a poor seal will result.

6. The small sleeve prepared in step 4 is then slipped over the wire and it is fused to the tungsten wire at one end, Fig. 78B. The glass is then collapsed and fused to the wire by rotating the wire and heating from the seal end toward the open end. One must be careful not to trap any air between the glass and wire during this operation. By employing the expedient of using a thin glass sleeve, one avoids over-oxidizing the tungsten wire because considerably more heat is required if a thick-walled sleeve is used.

The bead formed with this sleeve is thin, Fig. 78C. When a good seal is obtained, the color at the interface of glass and wire ranges from *golden yellow to reddish-brown*. If the interface is black, the wire had been oxidized too much before sealing with glass. Prolonged and successive heat treatments are then required to dissolve the oxide in the glass. It is not advisable to use a blackened seal.



Fig. 79

7. If the wire with the thin glass bead is to be used as a single-contact wire through the end or side of a glass tube, more glass must be accumulated on the thin bead to give a sufficient amount of glass for the final seal. This is done by using the same type of glass in the form of a thin rod. One end of the rod is attached to the end of the bead. The rod is then wound and fused to the thin-walled bead as illustrated

in Fig. 78D. The rod is cut in the burner flame when enough glass is accumulated and the glass is fused to a pear shaped bead, Fig. 78E. The bead with the wire is then kept hot by placing it on the screen of the Argand burner. The opening which is made in the tube of the same type glass is slightly smaller than the maximum diameter of the bead. The bead is held over the opening as the glass of the tube and bead are fused sufficiently to allow it to flow together. The seal is then annealed.

In pinch press construction, the tungsten wire requires only a thin glass layer and any dead wires must have the one end covered and closed with the seal glass as illustrated in Fig. 78F. The glass tube for the press is prepared as previously described. The opening in the tube slot should be wide enough so that all wires can be uniformly spaced. The wires are then mounted in a wire holder, Fig. 95, and the beads are located and held in the tube slot so that a short section of the bead glass will extend beyond both ends of the press. The flat portion of the tube is then heated and, when the glass is sufficiently fused and collapsed against the beads, it is pressed together with a forceps to insure a good seal between the bead glass and the flat end of the tube. The finished seal is shown in Fig. 78G. The entire assembly is carefully annealed.

Tungsten, beaded with Corning glass 778, sealed into Nonex 772, has been very successful as glass-to-metal seals. If a tungsten bead is required in a Pyrex system, a graded seal is required. Such a seal is used in the apparatus shown in Fig. 79. In this case tungsten wire was beaded with glass 778 and sealed into a tube of glass 772, a narrow band of uranium glass 3320 was then sealed to the Nonex 772 tube, and the assembly was then sealed into Pyrex. The recommended sealing order is: Tungsten, glasses 778, 772, 3320 and Pyrex. Glass-to-tungsten seals with glass 3320 have been successful. Glass 3320 can be sealed directly to Pyrex.

Pyrex-to-tungsten seals are impracticable except when the tungsten wire has a diameter of 0.015" or less. Even then it is preferable to bead the wire with Corning glass 7051 before it is sealed into Pyrex.

An example of a tungsten-to-glass seal is shown in Fig. 80. The large tube contains two 0.09" tungsten rods which were beaded with Corning glass 778. These beaded rods were pressed into a tube with a 4" flare of Corning glass 772. The glass blower is sealing the flare into a large bulb of 772 glass. Two sets of rollers are being used to distribute the weight of the large bulb.

A common type of Pyrex thermoregulator, particularly useful in controlling constant-temperature baths, is illustrated in Fig. 81. The essential parts of this regulator are the two contact points. The contact point in the glass-to-

metal seal is a tungsten wire. A length of braided copper is butt-welded to the tungsten wire so that a flexible connection can be made. The tungsten is covered with a sleeve of Corning glass 7051 by the procedure outlined for beading tungsten and the bead is made of Pyrex. The bead is sealed into Pyrex. The stopcock on the side arm is convenient for filling the regulator. It is not necessary, however, for the regulator can be filled through the capillary. By varying the



Fig. 80

size and shape, other forms of thermoregulators can be made with increased sensitivity. If a mercury reservoir is used, toluene, or a mixture of ethanol and water of 50 parts of each or any other suitable liquid can be used.

A series of contacts is sometimes required in a thermoregulator. These contacts may be made in the form illustrated in Fig. 81B. This glass-to-metal series can be made by using a soft glass capillary tube and platinum wires. The capillary tube is cut and a short piece of unbeaded wire

is laid across the glass wall. The capillary tubes are then sealed together. Successive seals are made in this way until all contacts are sealed into the tube. Extreme precautions must be taken when the glass is heated. The assembly must also be carefully annealed. The tube with multiple contacts can be used on any desired thermoregulator.

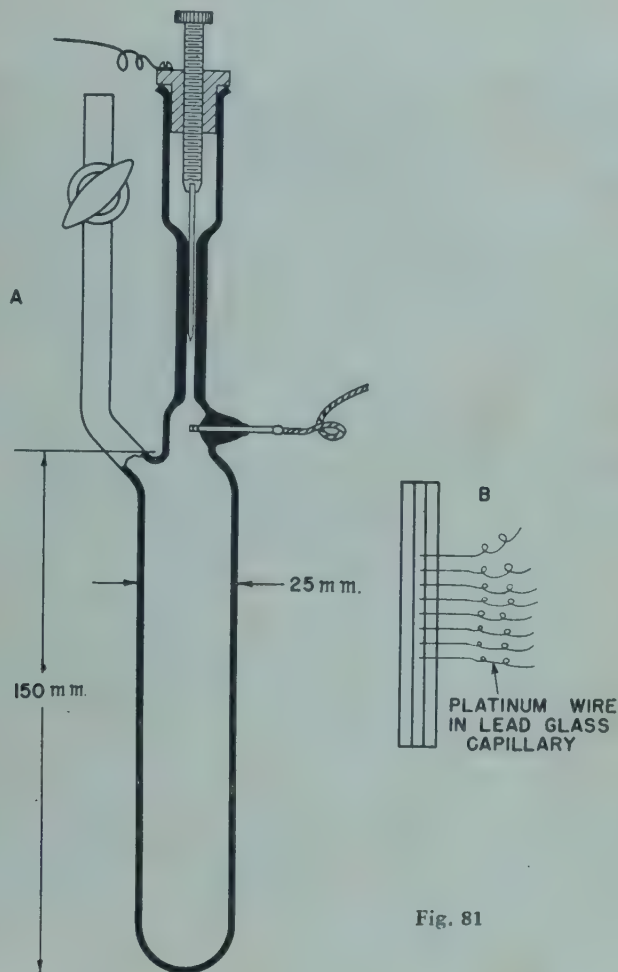


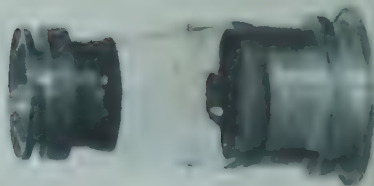
Fig. 81

MOLYBDENUM

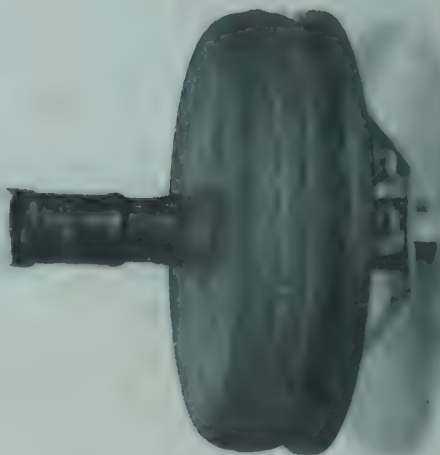
Molybdenum has not been extensively used for glass-to-metal seals because this metal has a tendency to oxidize very rapidly as seals are made. The oxide layer becomes thick quickly under oxidizing conditions. This oxide forms a non-adhering semi-liquid layer with the glass and poor seals are obtained. When molybdenum is required for glass-



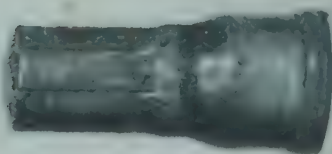
A



B



C



D



E

to-metal seals, Corning glass 706 should be used. A long close-fitting sleeve of this glass should be made for beading purposes and oxygen should be excluded as much as possible during the sealing operation. Molybdenum rods up to 10 mm. in diameter have been sealed to glass. Such a seal is shown in Fig. 82A. The sleeve in this seal is 3 inches long.

COPPER

The methods in sealing copper to glass were developed by William G. Housekeeper.⁴ These glass-to-copper seals are unique because the coefficient of expansion of the glass can be considerably different from that of copper. This metal has a temperature coefficient of expansion of 162×10^{-7} per degree C., and under certain conditions it can be sealed to Pyrex which has a coefficient of expansion of 32×10^{-7} . A large surface of contact is provided between the glass and copper and the latter is so proportioned in the seal that the stresses resulting from the different coefficients of expansion are less than the ultimate strength of the joint between the glass and copper.

Four types of seals will be described.

1. Copper wire can be sealed into glass if it is flattened so that the portion which is sealed to the glass is not over 0.002" thick. This flattened wire should be sealed by the pinch press method, but without using the preliminary thin-sleeve beading procedure because of the danger of over-oxidizing the wire. The glass of the press is first shaped by drawing down and collapsing a tube to form a shoulder and a section of tubing with a smaller diameter. The wall thickness of the shoulder and small tube should be the same as that of the original tube. The tube with the smaller diameter is cut with the burner flame. A section $\frac{1}{2}$ " from the shoulder is adequate for the press seal. This short section is heated and pressed together until the opening in the pressed glass is just large enough for the flattened wire. The clean flattened wire is pre-oxidized by heating to red heat for several seconds; then it is cooled, dipped into a solution of borax and water, dried in the flame or a furnace and laid into the open press. One end of the wire should be clamped into a pin vise so that it can be held in place. The glass is then fused and pressed together to give a good seal between the glass and metal. The finished seal is illustrated in Fig. 83A. It should be noted that the seal is made on the flattened portion of the wire. The assembly is carefully annealed. The borating step is helpful in preventing over-oxidation of the copper. Vacuum-tight seals have been made without borating the copper surface, but whenever the copper comes in contact with the burner flame during the sealing operation, it has been advantageous to prevent over-oxidation by covering the copper surface with borax.



A



B



C



D



E

2. Copper ribbon seals are made by a procedure similar to that of sealing wire to glass (in reality the flattened copper wire is a ribbon section). Copper ribbons up to 25 mm. wide and 0.015" thick have been sealed into Corning glass 008. The ribbon seal, however, requires one additional operation which was not necessary in the wire seal. The edges of the ribbon should be filed until the two sides have angles of $9^{\circ} \pm 1^{\circ}$. A cross-sectional view of the ribbon is given in Fig. 83B. This ribbon is heated to a red heat for

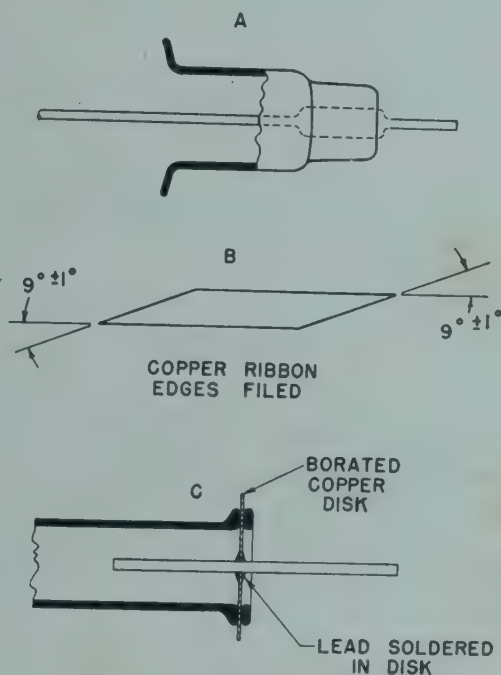


Fig. 83

about three seconds, borated and sealed into a prepared press.

3. Flat disks of 28 gage copper can be sealed to glass if the glass does not extend around the edge of the disk. An example of a disk seal is given in Fig. 83C. The disk is cleaned, pre-oxidized by heating for three seconds and borated. The ends of two tubes are then fused to the copper assembly is rotated in the burner flame. If only one tube is disk by holding the latter between the two tubes while the sealed to one side of the disk, it is advisable to seal a band of glass around the other. The glass on either side should not be sealed over the edge of the disk. The assembly is annealed when the seals are completed.

Vacuum-tight disk seals are quite useful if considerable current flows through the seal. Heavy copper rods which

are capable of carrying currents up to 100 amperes can be brazed through the disk before the seal is made.

4. The glass-to-copper tube seal is frequently used in the laboratory. It can be used in place of a graded seal because Pyrex can be sealed to one end and soft glass to the other. The tube of Fig. 84C is a seal of glass 772 to copper to soft glass.

The glass-to-copper tube seal may be made as an external seal where the glass is sealed to the outside of the tube, Fig. 85A. In an internal seal the glass is sealed to the inside

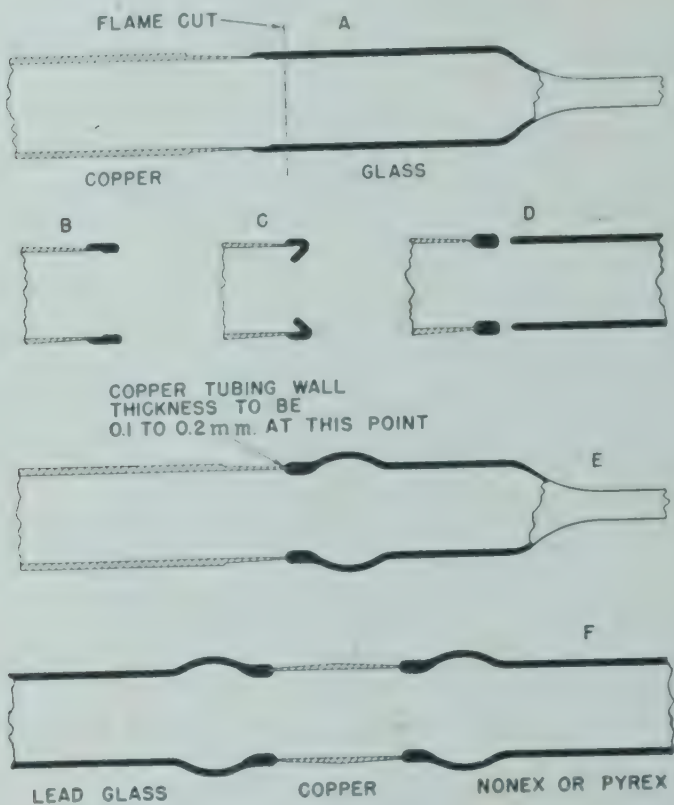


Fig. 85

of the tube. The most successful seal is a combination of the internal and external as illustrated in Figs. 85E and 85F. All seals are made on the copper tube which has been machined to a thin or commonly-called "feather" edge. The procedure for making an internal-external seal is as follows:

1. The copper tube is machined at the end to a thin edge. It is then mounted in a glass holder. The thin edge of the copper is heated red hot in a gas-air flame and a glass tube which fits snugly over the edge is pushed over the hot end.

The copper should not be allowed to cool because the copper oxide will flake. The glass is then fused to the copper without occluding air. The flame should be kept away from the metal during this operation. When the seal is finished the glass tube is cut in the burner flame about $\frac{3}{16}$ " from the end of the copper tube as indicated by the dotted line in Fig. 85A. After the glass tube is cut, the end should appear as shown in Fig. 85B. The glass is then heated and tooled down (Fig. 85C) with a flat carbon tool. It is then tooled into the tube with a round carbon tool. The finished glass covered end should appear as illustrated in Fig. 85D. A second glass tube is then sealed to the glass covered end by the procedure outlined for butt sealing, Fig. 85E. If the tube is machined at both ends, the seals illustrated in Fig. 85F can be made. This assembly can be used for sealing Pyrex to lead glass equipment. The two different glasses can be identified by the color of the glass-to-copper seal: with lead glass, the glass-to-copper is red at the interface of metal and glass; with Pyrex it is yellow. A Pyrex-to-copper cup seal is shown in Fig. 82D. The glass-to-copper tube seals are not limited to small sizes. Many good seals have been made on copper tubing up to 6" in diameter.

Heavy copper conductors in glass-enclosed bulbs capable of withstanding thermal shock have been quite useful for the construction of ultra-high-frequency transmitting tubes. Examples of sealing a copper rod assembly to glass are illustrated in Fig. 86. The copper rod may be brazed or welded to the part which is sealed to the glass sleeve, Fig. 86A, assembled in a pressed fit, Fig. 86B, or by machined screw threads as illustrated in Fig. 86C. The glass-to-copper seal is made as follows:

1. The copper is machined to a thin or feather edge.
2. A glass tube with an outside diameter which fits snugly into the tube is flared as illustrated in Fig. 86E.
3. The copper rod is then mounted on a suitable holder and the thin edge is oxidized by heating it red hot. This is done by rotating the copper in a cross fire.
4. The flared glass is then pushed into the hot opening and the inside and outside are tooled as it is fused against the copper, Fig. 86F.
5. When the glass-to-copper seal is complete, the glass is sealed to the remainder of glass tube assembly. The seals are then carefully annealed.

The glass-to-copper tube seal is mechanically weak because the copper must be thin enough to keep the stress on the glass within safe limits. The copper near the glass seal must never be overheated because it will oxidize to a degree where it will be porous. The mechanical strength of

the thin copper is also decreased still further under such treatment. If glass-to-copper tube seals are subjected to thermal cycles (heating and cooling) the thin copper may fail because it is being continually work-hardened. Copper seals cannot be used with mercury because the latter will

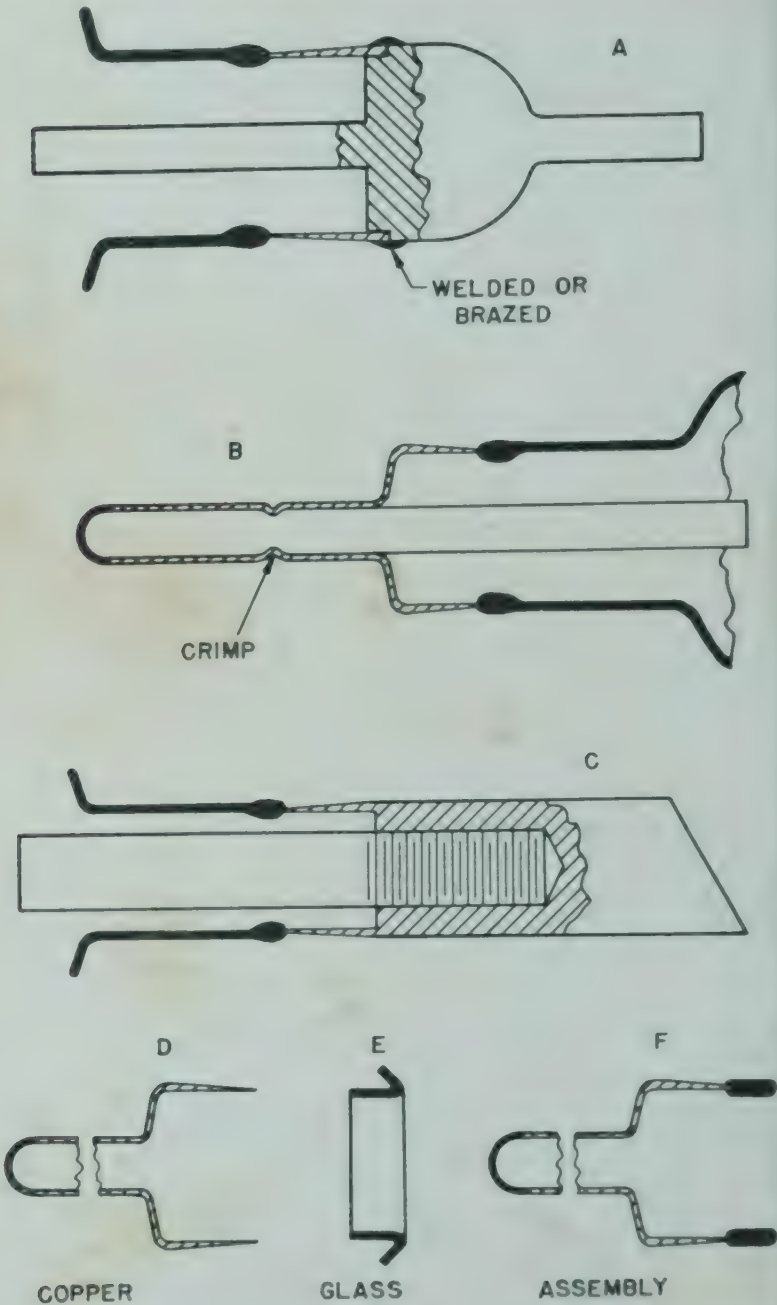


Fig. 86

amalgamate with copper. However, copper can be electroplated with a suitable metal after the seal is completed. The tube in Fig. 82E was nickel-plated after the seal was made.

Machining a copper tube end to a thin edge is sometimes quite difficult unless a metal backing is used to reinforce the tube. A tight-fitting plug can be made which fits into the tube. An alloy, Cerrobend,¹⁰ is also useful for reinforcing a copper tube. This eutectic alloy has a melting point of

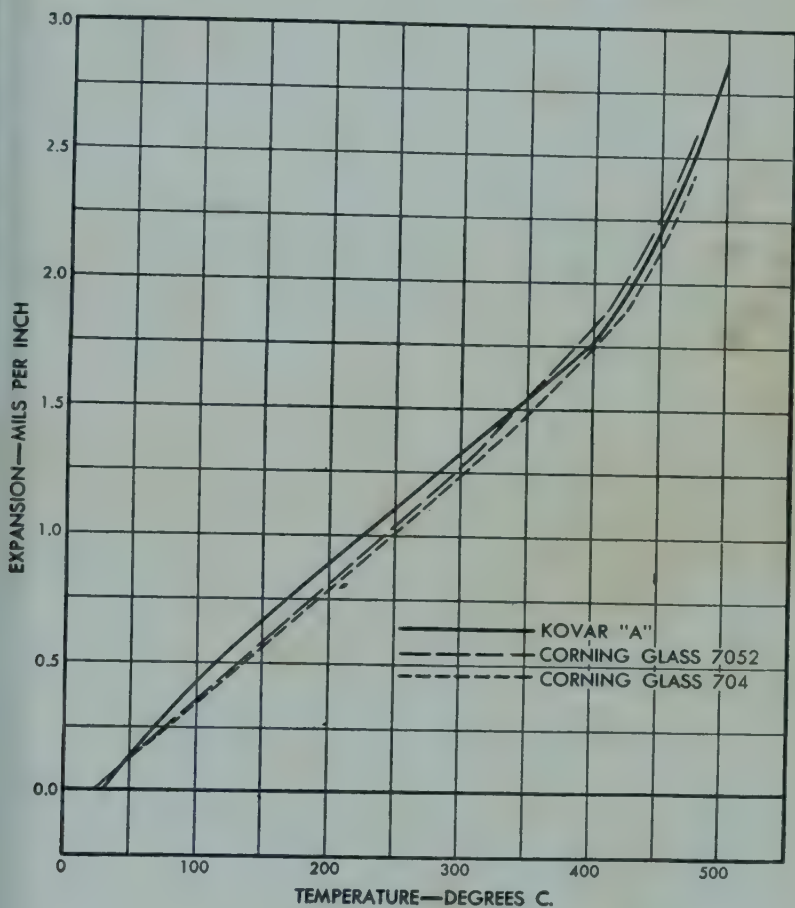


Fig. 87

160°F. and does not adhere to the copper. It is melted and poured into the tube which is machined after the alloy has hardened. After the machining is complete, the alloy is removed by melting.

DUMET

Dumet as described by B. E. Eldred² is made by coating a billet of nickel steel with copper and drawing the coated billet to a wire. The nickel-steel core of the finished wire

contains 38% nickel and about 20% to 25% by weight of copper. This wire is still used extensively in lamps and vacuum tubes.

The temperature coefficients of expansion of Dumet are approximately as follows:

Radial, $80-100 \times 10^{-7}$ per °C.
Axial, $61-65 \times 10^{-7}$ per °C.

From these coefficients of expansion it can be seen from Table 11 that the seal will be badly strained when G-5 glass is used. Seals with this glass have been successful because the low yield point of copper sets a limit to the stress exerted. The wire, 1 mm. or less in diameter, is satisfactory for glass-to-Dumet seals. Lead glass, G-5, can be used for beading this wire. It is beaded by the same procedure outlined for making glass-to-metal seals with platinum. Since Dumet is comparatively expensive, it is only used in lengths necessary for the glass-to-Dumet seal. Lead wires of nickel and copper are butt welded to the two ends of the Dumet wire for the press welds.

KOVAR

Kovar, a nickel-cobalt-iron alloy, was developed and perfected by the Westinghouse Electric Corporation. It, and the alloy Fernico which is used by the General Electric Company, have a specific temperature coefficient of expansion which is nearly the same as some of the standard glasses. A comparison of the thermal expansion of Kovar with Corning glasses 7052 and 704 is shown in Fig. 87. The specific properties of Kovar are given in Table 14.

TABLE 14. SPECIFIC PROPERTIES OF KOVAR

Composition.....	29% nickel, 17% cobalt, 0.3% manganese, 52% iron
Melting Point.....	Approximately 1450°C.
Density.....	0.302 lbs. per cubic inch
Hardness, Annealed.....	760°C. 140 to 160 B.H.N.
Hardness, Unannealed..... 200-250 B.H.N., depending on degree of cold work.
Electrical Resistivity.....	49 Microhms (cm. ²) (cm.)
Thermal Conductivity.....	0.046 calories/(cm.) (sec.) (°C.)

Since Kovar has thermal expansion properties which are very close to those of several standard glasses, the alloy need not be machined to feather edges as previously described for copper. This alloy can readily be machined for glass-to-Kovar seals. The sealing surfaces should be free from marks or scratches which extend across the sealing surface. (Other marks are not objectionable.) Glass should not be sealed to surfaces of Kovar parts which have sharp corners; the edges should be rounded with forming tools.

Kovar sealing surfaces must be thoroughly clean and free from gas or gas-forming components. If the surface is not degassed before sealing to glass, gas bubbles will form at the glass-metal interface as the seal is made. These bubbles will impair the mechanical strength of the seal. Kovar is degassed by heating it in a furnace to a temperature of 1050°C . for a period of 20 minutes. Hydrogen which is bubbled through a water trap is fed into the furnace to maintain a hydrogen atmosphere. The metal is moved to a cooling section of the furnace and cooled to 300°C . before it is removed from the furnace. Degassed Kovar should not be touched with the hands—especially the surfaces which are to be used for the glass seal. Glass-to-Kovar seals should preferably be made within three hours after the alloy is degassed.

Kovar must be oxidized before glass can be sealed to it. This alloy may be oxidized during the sealing operation by heating it to about 650°C . in the oxidizing portion of the burner flame, or, it may be pre-oxidized in a furnace. The degree of oxidization for good seals is difficult to determine and a procedure of obtaining a suitable state of oxidation is best gained by experience. Heavily oxidized Kovar yields mechanically strong seals, but these seals are not vacuum-tight. Under-oxidized Kovar yields hermetic seals which are mechanically weak.

If the Kovar is oxidized in the burner flame, 7052 glass is sealed to the alloy while the temperature of the alloy is still between 650 and 800°C . The glass is fused and attached to the metal. If the seal is small, the glass and Kovar, which is suitably mounted, can be worked by hand. Larger seals are best made by using a glass blower's lathe. A new procedure of applying glass to Kovar has been developed by engineers of the Westinghouse Lamp Division.¹² The oxidized Kovar surface which is to serve as glass-to-Kovar seal is covered with powdered glass by suspending the latter in a suitable solvent and spraying the mixture on the Kovar. The metal and glass are then placed in a furnace and heated until the powdered glass is fused to smooth film on the Kovar. Glass can then be sealed to the glass on the Kovar by the simple procedure of fusing glass-to-glass. The glass-to-Kovar seal is not affected by the second sealing operation.

Annealing Glass-To-Kovar Seals

When glasses 704 or 7052 are used with Kovar, seals can be obtained which are nearly stress-free by the annealing technique previously described for annealing glass-to-glass seals. The seal is heated to dull red heat in the annealing burner and covered with a deposit of carbon by turning down the air supply to the air-gas annealing burner.

Furnace annealing is accomplished by heating the seal to 484°C . and maintaining this temperature for twenty min-

utes. The temperature is then lowered 1°C . per minute to 450°C .; and then about seven to ten degrees per minute to room temperature.*

The oxide on Kovar surface must be removed after the glass-to-Kovar seal is made if the alloy is to be soldered, welded or brazed. A solution of 10% HCl and 10% HNO_3 in water, heated to 71°C . (or 160°F .) can be used for cleaning the oxidized surface. The Kovar is immersed in this solution for five minutes, washed thoroughly with water and dried.

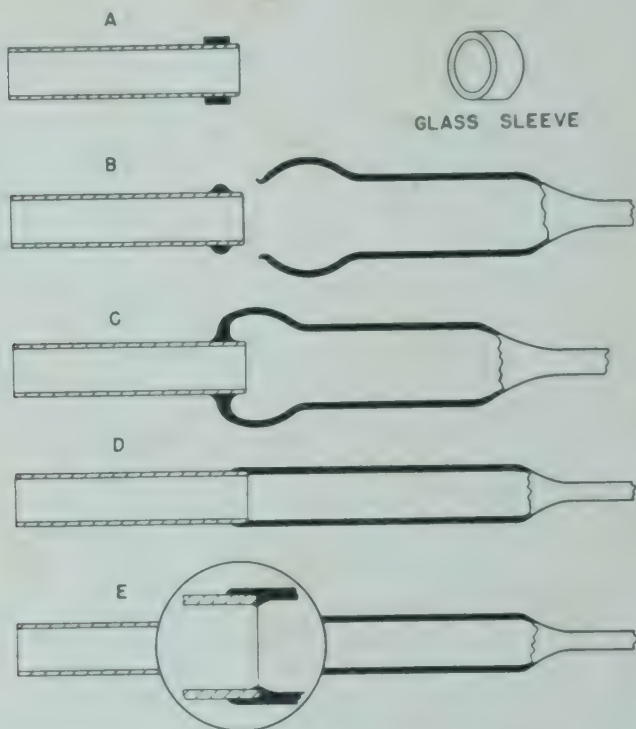


Fig. 88

Kovar can be welded with an electric arc. The electrodes should be of the fluxed cooled type and of "18-8" stainless steel (with 18% chromium and 8% nickel). When welds are made on Kovar which has glass seals, one should remember that the metal will conduct heat more rapidly than the glass. The alloy, between the glass seal and the position which is to be welded, must be cooled to prevent heat from flowing too rapidly to the glass seal. The glass and Kovar can also be heated to prevent uneven heating during the welding operation.

Kovar is copper-brazed by using pure copper on the clean alloy surface. A small piece of copper is placed on the alloy

surface and the two are placed into a hydrogen-atmosphere furnace. The Kovar is heated from room temperature to 1100°C. in one hour* and this temperature is maintained for 15 minutes. The hydrogen performs as a flux.

Kovar can be obtained in rods, wire, tubing, sheet or special forms, such as cups, flanged cups and flanged eyelets. Stupakoff Ceramic & Mfg. Co., Latrobe, Pennsylvania, is the distributor of this alloy.

Procedure for Making Glass-to-Kovar Seals

As an example of making a glass-to-Kovar seal, a description of the procedure for sealing glass to a Kovar tube will be described.

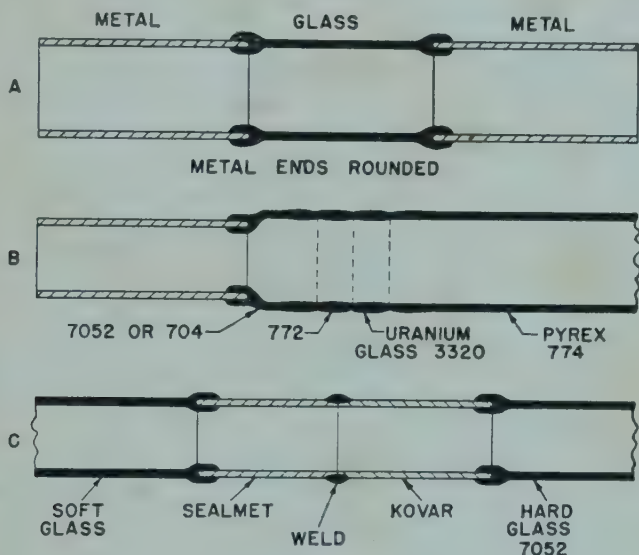


Fig. 89

1. A band of Corning glass 7052, 6 mm. in length, is cut from the glass tube which has a diameter just large enough so that the small section can be slipped over the Kovar tube, Fig. 88A.

2. A point is drawn on a tube of Corning glass 7052. The tube should have the same diameter as that of the glass band, or it can be drawn down from a larger tube and cut open in the burner flame. The end must also be expanded to a bulb and opened if a small tube is used.

*EDITOR'S NOTE.—Only in factory production, with high-precision automatic temperature-time control systems, can these recommendations be met *exactly*; most readers would have to rely on all-purpose laboratory furnaces. However, two or three degrees more or less at the holding temperature, and a few minutes longer or shorter in the controlled rate-of-change periods, will not matter.—M. F. Behar.

3. A short section of Kovar tubing, which has been degassed under conditions previously described, is mounted on a glass holder with asbestos tape. The sealing surface should be clean and the tube should not be handled at the sealing surface.

4. The Kovar is then oxidized by heating it to a dull red heat. It is removed from the flame and allowed to cool slightly.

5. The short section (6 mm.) of 7052 glass tubing is slipped over the oxidized Kovar tube and a small spot of the glass is fused to the alloy tube to prevent it from slipping. Fig. 88A. The tube is then rotated until the glass is fused sufficiently so that it can be tooled against the Kovar. One must be careful not to occlude any air between the glass and metal interface as the seal is made. To avoid this, it is best to start to tool the glass at one end and gradually work the glass against the metal until the other end is reached. In Fig. 88B the seal is shown well back from the edge of the tube.

6. The glass tubing is then sealed to the bead glass which is sealed to Kovar by the technique of making a glass-to-glass seal, Fig. 88C. The seals are then annealed by heating in the annealing burner flame, or in an annealing furnace, according to the procedure previously outlined.

Two other seals are shown in Fig. 88D and 88E. The seal glass in Fig. 88D extends to the end of the Kovar tube, while in Fig. 88E the glass extends over the end of the rounded edges of the tube.

The seal illustrated in Fig. 89A is a combination of an internal and external seal. The seal glass is worked over the edge of the Kovar much in the same manner as was described in sealing glass to a copper tube.

If the glass-to-Kovar seal is attached to Pyrex, a graded seal must be made between the 7052 glass and Pyrex. This graded seal is made by starting with a Pyrex tube. This tube is drawn to a point and allowed to cool. The Pyrex tube is then opened at the opposite end with the flame. A tube of uranium glass 3320 is butt-sealed to the Pyrex tube with a minimum of working the two glasses. The seal should be thin. The uranium glass is then cut 4 mm. from the seal. A tube of 772 glass is sealed to the uranium glass and the tube of 772 is cut with the flame 4 mm. from the second seal. The graded glass seal is then sealed to the 7052 glass tube, Fig. 89B. A glass-to-Kovar seal with a graded seal is shown in Fig. 84A and Fig. 82B. The same glass-to-Kovar seal is shown in Fig. 84B. In this example, however, the glass-to-Kovar seal was made so that the Kovar tube extends beyond the glass-to-Kovar seal. The glass tube has a small bulb beyond the 7052 glass seal. The seals

illustrated in Figs. 84D and 84E are made of glass 7052 and Kovar.

A method of connecting soft glass to Pyrex is illustrated in Fig. 89C. A tube section of Sealmet is welded to Kovar. Soft glass is sealed to the Sealmet and 7052 glass is sealed to the Kovar by procedures outlined above.

Another example of glass-to-Kovar seals is illustrated in



Fig. 90

Fig. 90. Here two seals of 7052 glass-to-Kovar are used to seal the top and extension tube of a trap to the body of the latter which is 7052 glass. The two graded seals of 772, uranium glass and Pyrex, are noticeable on both the inlet and outlet tubes.



Fig. 91

A Kovar-to-glass, 7052-to-Kovar, is illustrated in Fig. 82B. An example of a method of connecting a small steel boiler to a Pyrex system is shown in Fig. 82C. The order of the various glasses and metal, top to bottom is as follows: Pyrex, uranium glass, 772 glass, 7052 glass, Kovar, and steel. The steel boiler is fitted with a circular electrical heater which is bolted to the flat bottom.

Kovar rods are frequently used as conductors through glass. An example of four large Kovar conductors through

a glass cap is illustrated in Fig. 91. The Kovar rods are fitted with special caps for the glass-to-Kovar seals. The tubulation in the center is used for evacuating the finished tube which will contain the four sealed conductors. The tubulation has heavy walls so that it can be tipped-off by fusing the glass.

Glass-to-Kovar seals have been made by using induction heating instead of a gas-oxygen flame. The high-frequency (40-60-kc.) current is supplied by spark or vacuum-tube generators. It is important that the glass and metal parts be in intimate contact because it is the Kovar which is heated by induction, and the adjacent glass is fused by the conduction of heat from the Kovar. This method is useful when it is desirable to make glass-to-Kovar seals on small Kovar parts. The fusion of glass is rapid and the control is quite easy.

Small glass-to-metal seals can be made by hand, but when large seals are required the glass blower must use a lathe. There are two distinct advantages in using a lathe for making large seals:

1. Large and cumbersome sections of glass and metal can be handled by the lathe and the glass blower can use both hands for tooling the glass and directing the flame over various sections of it.

2. The glass and metal are truly centered in a lathe to produce precision seals.

The popular Litton lathe, Model EE¹³ is shown in Fig. 92. The head stock at the left is synchronized with the tail stock at the right. The Litton cross-fire which is being used is adjusted in the form of an arc which covers nearly one-half of the circumference of the glass. This burner can be moved, either to the left or right, by the hand wheel behind the burner. The operator is tooling glass against a Kovar surface.

SEALMET

An alloy which contains 51.55% by weight iron, 42% nickel, 6% chromium, 0.12% silicon, 0.29% manganese and 0.04% carbon was developed by the Higrade Sylvania Corporation.¹⁴ This metal has a thermal coefficient curve very close to that of Corning glass number 001. This glass is used in making glass-to-Sealmet seals and the glass is then sealed to the envelope of Corning glass 008. The procedure for making glass-to-Sealmet seals involves techniques very similar to those described for Kovar. Technical data concerning Sealmet can be obtained from the Allegheny Ludlum Steel Corporation, Pittsburgh, Pennsylvania.

PRODUCTION OF LAMPS AND TUBES

The production of lamps and tubes by machines has been

developed to the extent that very few are made by hand for commercial use. Experimental lamps or bulbs, however,



Fig. 92

are sometimes required in the laboratory. Since it is not economical to invest in production machines for laboratory work, the procedure for making lamps and tubes by hand will be described.

Two methods can be used for sealing electrodes into tubes. The electrodes are either bead-sealed into the lamp or tube-flare or press-sealed into the glass of the flare. The number

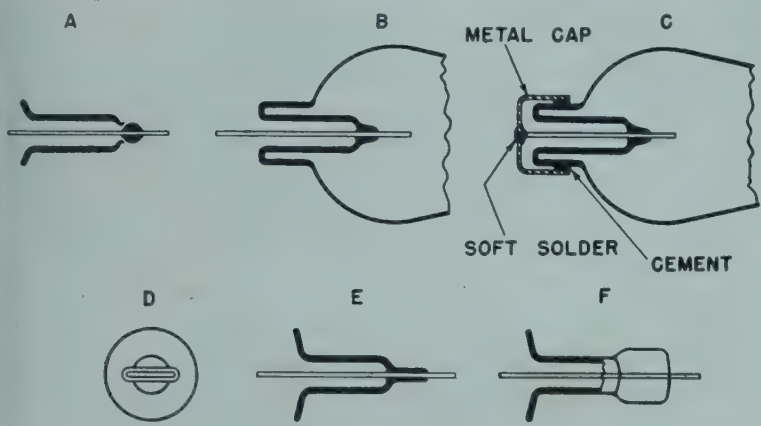


Fig. 93

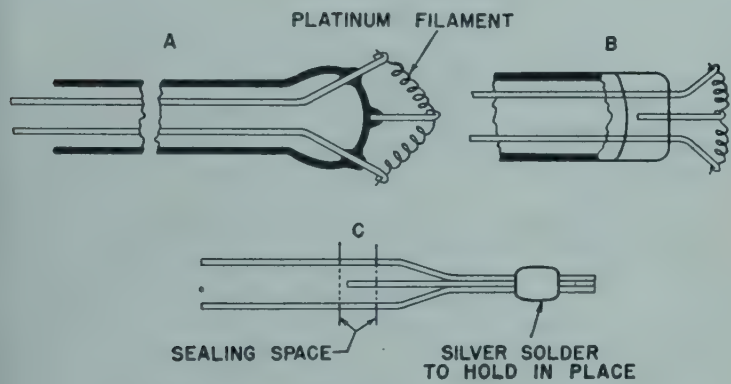


Fig. 94

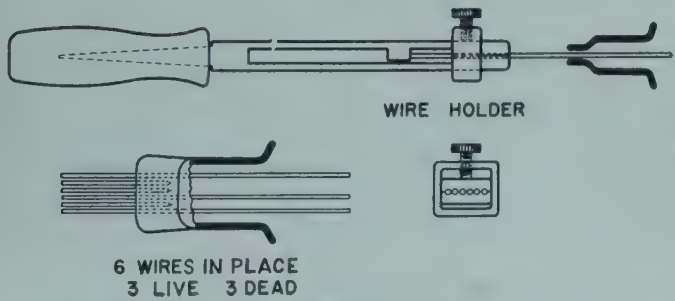


Fig. 95

of electrodes which can be sealed into a flare will depend on its size.

Single-wire electrodes are made as follows:

1. The flare is made by pulling a point on a tube with

the required diameter. The flare is formed on the opposite end by the procedure outlined in Chapter II and illustrated in Fig. 39.

2. This flare is mounted on the glass tube with asbestos tape; the opposite end is shaped for the seal. If the bead seal is used, the opening is made by pulling the tube to a cone and opening this cone. The flare is illustrated in Fig. 93A. The wire is then beaded by the procedure recommended for the type of wire used and the glass bead is sealed to the flare. The assembly is carefully annealed and then sealed into the bulb or tube, Fig. 93B. The electrode is soft-soldered to a cap after it is cemented to the tube, Fig. 93C.

The press seal is used almost exclusively in commercial production because it is more easily made in machine production.

1. The flare is made with a triangular tool as described above. This flare is then mounted on a glass tube and the end of the flare-tube is fused and pressed until the end has a form shown in Fig. 93D.

2. The wire is then placed into the glass end and the glass is fused and pressed against the wire. The press seal when correctly made will appear as shown in Fig. 93E and F. The seal is carefully annealed.

3. The flare is then sealed into the tube by a procedure of sealing a flare to a tube. The electrode is then soft-soldered to a cap which is cemented to the tube.

Multiple electrode seals are used more extensively for laboratory installations. Beaded wire electrodes are more difficult to make, especially if several are sealed through the same flare. It is more convenient to use the press seal because the wires can be spaced more easily. As an example of the two types of seals, the production of the flare for a combustion pipette will be described. The electrode assembly consists of two lead wires and a wire support.

The beaded electrode flare is made as follows:

1. The tube for the beaded electrodes is made by blowing a bulb on the end of the tube. This bulb will allow more space for the glass-beaded wire. Two electrodes are beaded by the procedures described in this chapter. Tungsten press welds may be used. These prepared beads consist of a small length of tungsten which is butt-welded to braided copper on one end and to a nickel rod on the other. The beading procedure has been described for making tungsten bead seals. The filament support has the glass beaded over one end. The three are then sealed into the glass and the filament is spot-welded to the leads (Fig. 94A) after the seals are annealed.

The press seal can be made in about one-third the time required for the beaded electrode seal. The press is made by

fusing the end of a tube and pressing it together so that there is just room enough to insert the electrodes. The electrodes and support are silver-soldered together so that each will be

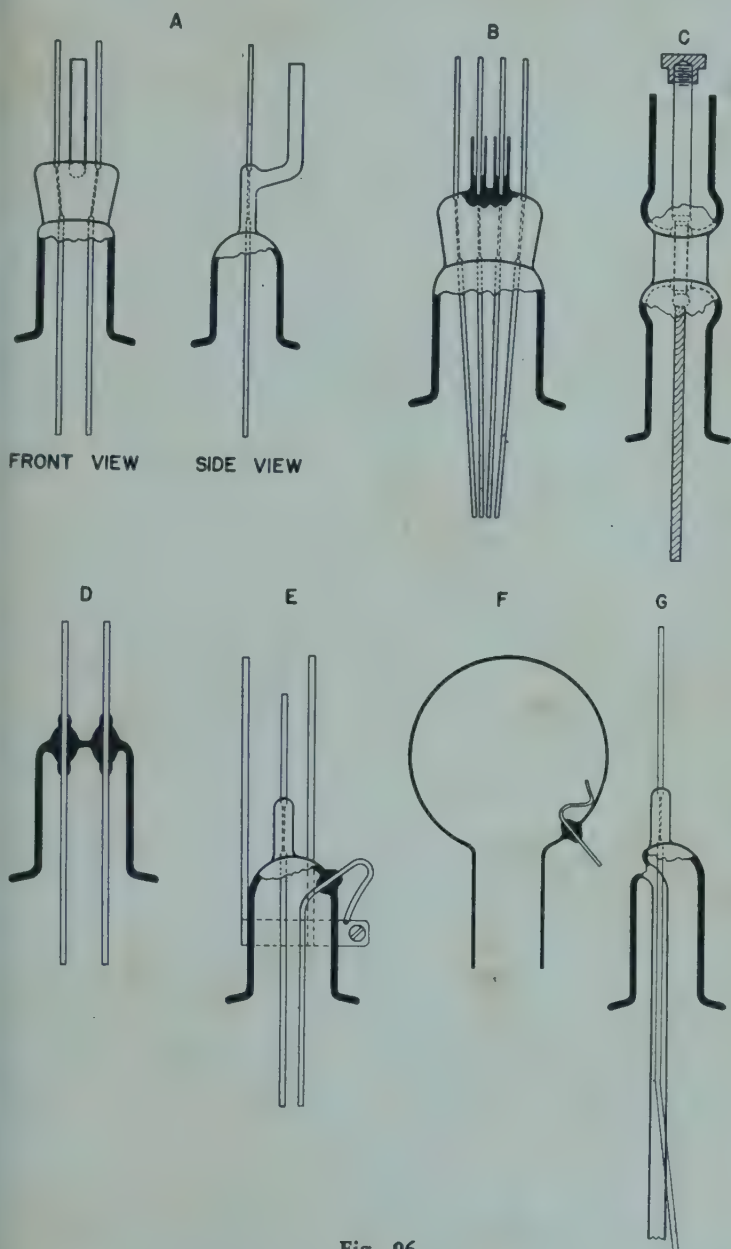


Fig. 96

held in place by one common holder, Fig. 94C. The electrodes are then put into the press so that the filament support extends to about the middle of the press. The glass is fused

and pressed against the electrodes. The assembly is then annealed. The silver solder is removed and the electrodes are bent to the desired angles. In bending electrodes, one should always hold the electrode near the seal with pointed pliers to avoid cracking the seal. The platinum filament is then spot-welded to the electrodes, Fig. 94B.

When a larger number of electrodes are to be press sealed into glass, it is convenient to use the simple wire holder shown in Fig. 95.

Various types of vacuum-tube stem mounts are shown in Fig. 96. The construction of these mounts consists both of the bead and press seals; and numerous modifications can be incorporated into specific assemblies by using construction details from several of the electrode arrangements. These mounts may be used with any of the standard glasses if the correct metal and sealing procedure is used.

Glass rod supports are sometimes convenient and may be sealed to press seals as shown in Fig. 96A. The side view shows the shape of the glass rod. It is best to seal the rod to the press after the wires are sealed in. The rod is straightened after the press seal is completed.

When two electrodes carry sufficient current to cause a short circuit by arcing, it is advisable to seal lengths of 3 mm. O.D. tubing above the seal. The press seal with insulating tubes is shown in Fig. 96B.

The seal illustrated in Fig. 96C is made by using a press weld sealing wire. The lower section is braided copper welded to a metal which can be sealed to glass. The upper section, containing the metal plate, is also made of a different metal which is press-welded to the short glass-sealing metal.

A simple two-electrode bead seal is illustrated in Fig. 96D. The seal glass which is beaded to the metal extends beyond both sides of the bead seal.

A convenient method of mounting a plate is illustrated in Fig. 96E. The clamp which supports the plate is fastened and held in position on the flare while the other electrodes are press-sealed through the end of the flare tube.

A lead which contacts the inner surface of a bulb is used in special photoelectric tubes. This electrode seal is illustrated in Fig. 96F. The electrode contacts the inside wall of a tube or bulb which is covered with a metal coating.

A hand-made "tipless press" is illustrated in Fig. 96G. A small thin tube is sealed into the flare. This tube is then used to evacuate the bulb after it is made. The procedure for making this assembly is as follows:

1. A special holder must be made as shown in Fig. 97A. The tube, which has a diameter equal to that of the proposed flare, is sealed to a smaller tube which has an inside

diameter of about 5 mm. The large tube section is then flared by the same procedure used in making the tube flare. The tip-off tube can then be held in place as illustrated.

2. The electrodes are press-sealed into the tube flare by using a spacer clamp or a wire holder. The tube-flare is

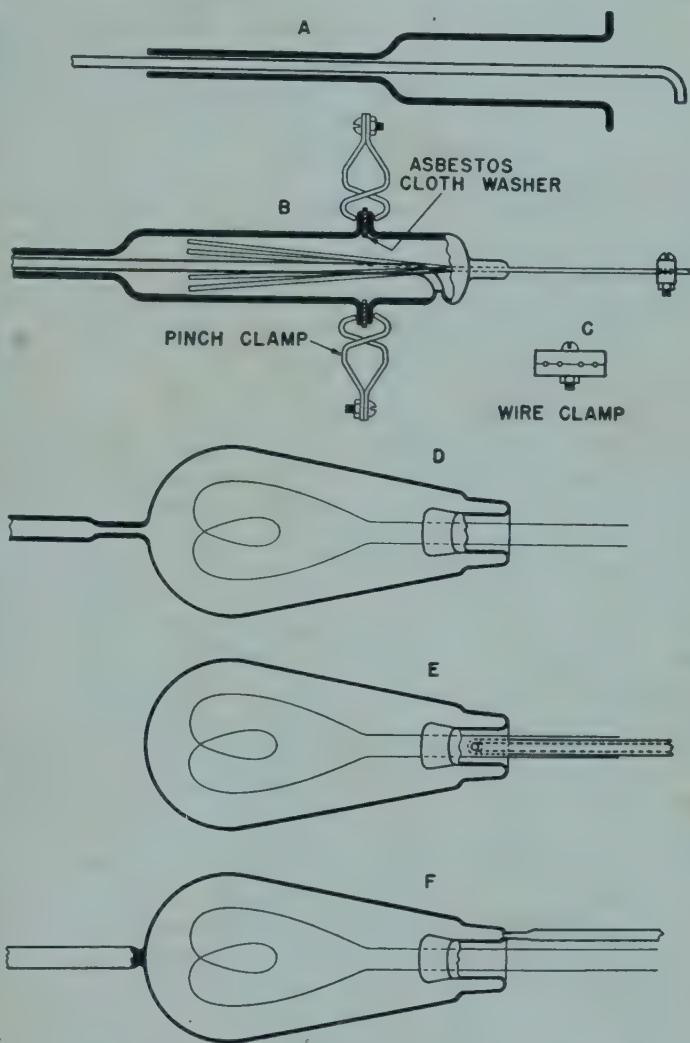


Fig. 97

then mounted on the tip-off tube holder as illustrated in Fig. 97B. The tip-off tube is then sealed to the inner wall of the flare. The glass over this small tube is blown out to a small bulb and collapsed several times to insure a good seal. The glass is then blown out to a thin bulb and the opening is fire-polished. When the flare is sealed to the

INFRA RED Heating Drying

SEEING

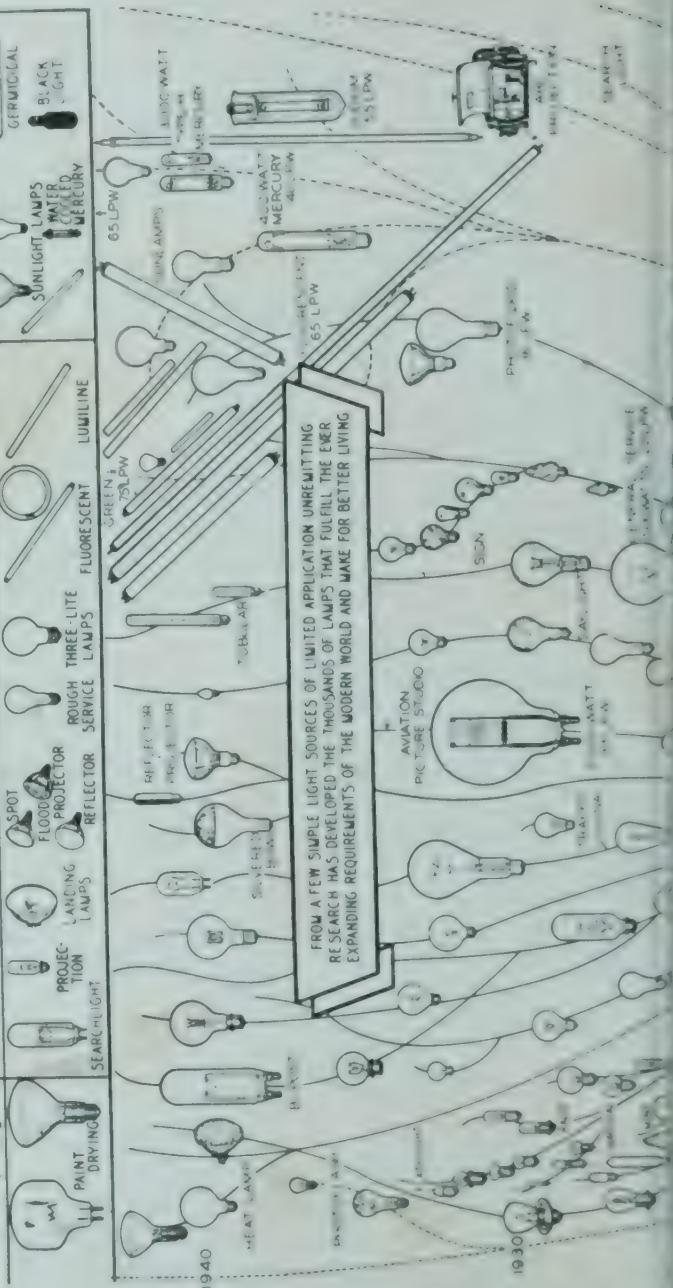
~~Luminous Efficiency~~ ~~Color · Contour~~
~~Optical Precision · Control · Adaptability~~ ~~Decoration~~

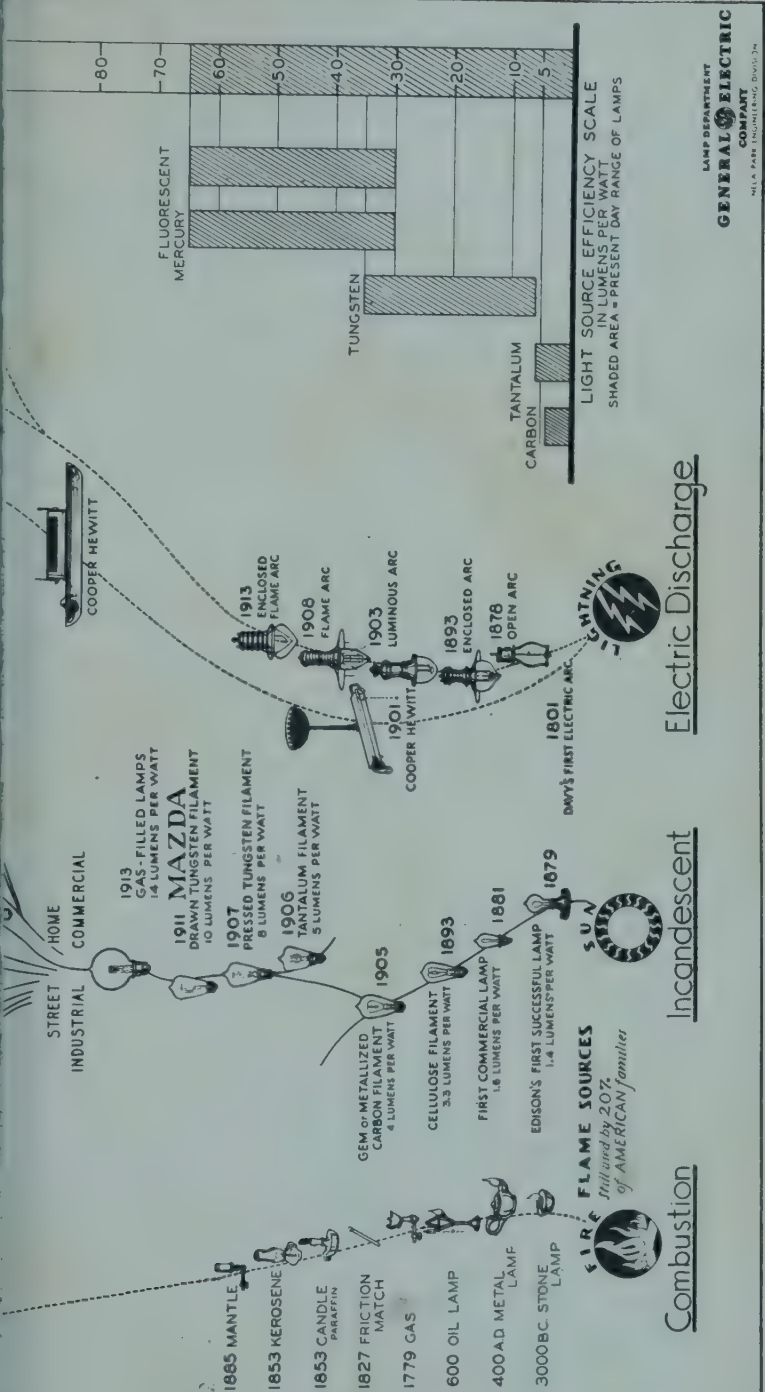
Decoración
Color · Contour:

ULTRA VIOLET

Suntan Germicidal
Photo Chemical-Fluorescent

Theoretical Efficiency of White Light





LAMP DEPARTMENT
GENERAL ELECTRIC
 COMPANY
 414 FIVE THUNDERING DRUMS DR.

bulb, the small tube is protected from the heat by slipping a quartz tube over the small tube.

Three types of tip-off tubes or tubulations are illustrated in Fig. 97D, E and F.

1. The tubulation at the tip of the bulb is given in Fig. 97D. The bulb is evacuated through this tube and it is then sealed by fusing and drawing the tube from the bulb. Although this type is quite convenient because the tubulation serves as a handle, it is not used in commercial practice at the present time.

2. The type shown in Fig. 97E has been discussed above.

3. The type shown in Fig. 97F is made by using a temporary blowing tube on the bulb and sealing a tube to the edge of the flare. The temporary tube is then removed and the bulb is worked to a smooth surface at this point. The bulb can then be evacuated through the tubulation and sealed by closing and drawing away the small tubulation at the edge of the flare.

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CHAPTER IX.

PRODUCTION OF HIGH VACUUM

High vacuum and equipment for its production played an important role in the commercialization of the x-ray tube, the incandescent lamp and radio tubes. Up to 1905 Toepler and similar pumps were used for evacuating x-ray tubes and lamps, but to meet the demands of increased production more rapid evacuating equipment was required. Gaede produced a rotary oil pump in 1905 which was capable of partly meeting the demand at the time. The advent of the Coolidge x-ray tube and the tungsten-filament incandescent lamp increased the demand for better high vacuum

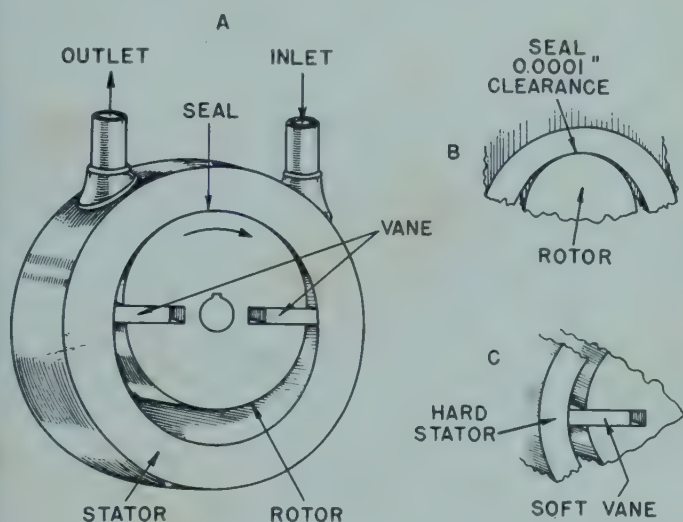


Fig. 98

equipment. The production of a successful mercury diffusion pump by Gaede¹ in 1915 and the more efficient and speedier condensation pump by Langmuir² in 1916 stimulated the development of many different pump designs. Since that time encouraging progress has been made in the production of metal commercial vacuum pumps.

The development of laboratory pumps—both rotary-vane and condensation—has paralleled the development of the larger commercial pumps. It was found more economical to build the smaller condensation pump of glass. The glasses available before 1915 were the high-expansion types and precautions were necessary in fabricating glass condensa-

tion pumps with multiple ring seals. Uneven expansion of the glass of inner tubes, which came into contact with hot vapors and outer water-cooled condenser jackets, made it necessary to seal one end of the outer water jacket with rubber tube sections. Pyrex glass No. 774, capable of withstanding greater thermal shock, has made it possible to build many different intricate pumps. Compact all-glass assemblies have been designed and several good pumps can be made by research workers who have a limited knowledge of glassblowing techniques.

Condensation pumps developed in various laboratories are all based on the same principle of pumping gas with a

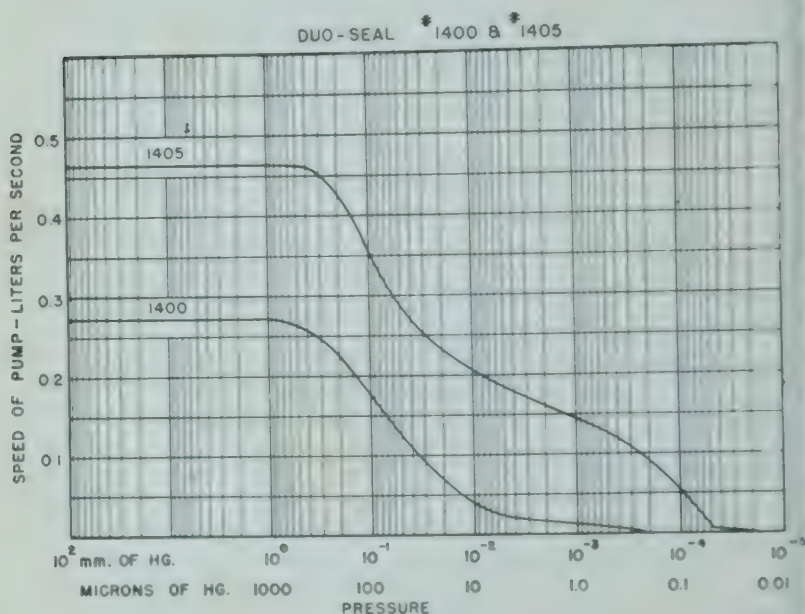


Fig. 99

rapidly-moving vapor stream. For a theoretical as well as experimental study of the factors involved in pumping gases with a moving vapor stream, the reader is referred to the work of P. Alexander³.

A complete discussion and description of every available means of creating vacuum is best made in a special treatise. It will suffice here to give details of the more common vacuum pumps which to the authors' belief are sufficient for nearly all laboratory studies. The equipment which will be discussed can in some cases be purchased from commercial producers.

ROTARY VANE MECHANICAL VACUUM PUMPS

The design of a common type of rotary pump, the Welch Duo-Seal pump is illustrated in Fig. 98A. The essential

parts of the pump are a cylindrical stator and a rotor which is fitted with vanes for moving the air or gas from the inlet to the outlet port. The rotor is positioned eccentrically in the stator and concentrically with reference to its own periphery. It is mounted on a shaft which extends through a packed gland in the side plate of the pump. The rotor is rotated by connecting the shaft directly to a motor with a suitable coupling or by a pulley and belt arrangement. The clearance between the rotor and the machined and hardened stator is in the order of 0.0001", Fig. 98B. The vanes are held against the stator by springs and, as the rotor moves, the vanes move in or out of the slots or guides, Fig. 98C. The mechanism is covered with oil and the wear on the vanes and stator is quite small.

The operation of pumping air or gas is quite simple. As a vane crosses the inlet port of the pump it traps the air which is between the stator and rotor and pushes the air out of the outlet port. Oil between the stator wall and the vane forms a good seal at the point of contact. This operation is repeated twice in each complete revolution of the rotor and from 300 to 600 times a minute. The pressure in any closed system which is connected to the inlet port of the pump is reduced to the ultimate vacuum limit of the pump, which may be from 0.001 to 0.00005 mm. of mercury. Check valves prevent the oil from flowing through the inlet to the evacuated system. The Welch Duo-Seal pumps can be obtained in single-stage or two-stage units. The latter is capable of pumping higher vacua because of the greater efficiency gained in two stages.

Another series of pumps for general laboratory work is supplied by the Central Scientific Company, Chicago, Illinois. The series consists of three pumps, the High-vac, Mega-vac and the Hyper-vac. The principle of pumping gases is similar to that of the Welch Duo-Seal pumps. A rotor is mounted concentrically with the stator but eccentrically with reference with its own periphery. The vanes are fitted into slots in the stator and are held against the rotor with springs. The gas is trapped between the stator and rotor as the latter passes the gas inlet port. This gas is forced through the outlet port as the rotor moves through one revolution. The vanes contact the rotor at all times and are located between the inlet and outlet ports. Suitable checks prevent the oil from flowing into the vacuum system.

The Leybold pumps, a Gaede series of vacuum pumps, are supplied by the James G. Biddle Company, Philadelphia, Pennsylvania. The pumping principle of these is similar to that of those described above.

The selection of the proper rotary pump will depend upon the type of work it is required to do. Pumps are rated as

having certain pumping capacities at each respective pressure and a study of these pumping characteristics is necessary to insure proper results before a pump is installed. Rotary pumps are used with condensation pumps for reducing the pressure to a suitable forepressure so that the condensation pumps can operate efficiently. However, if the



Fig. 100

speed* of the rotary pump is not high enough at this backing pressure the efficiency of the condensation pump is reduced. Suppliers of rotary pumps have exhaustive data concerning the performance of their pumps at various pressures and these data should serve as a guide when a pump is selected. The performance of the Welch Duo-Seal pumps 1400 and 1405 is given in Fig. 99. The speed of both pumps is constant over the pressure range of 100 to 1 mm. mercury and decreases to the ultimate vacuum of each pump.

Oil rotary pumps are usually abused when they are used for a general purpose pump. The oil is not changed frequently enough and the pump must operate in a heavy sludge which is formed, when dust, water vapor and corrosive gases are pumped. Suitable traps should always be installed on the inlet side of the pump. These traps should have large leads and should contain chemicals to scrub the undesirable constituents from the gas before it enters the pump.

CONDENSATION VACUUM PUMPS

It has been pointed out that rotary pumps are capable of pumping vacua up to about 1.0 to 0.01 mm. mercury at suitable speeds. If higher vacua are desired a condensation pump must be used in series with a rotary pump. The latter reduces the pressure to what is called either a backing or forepressure. The condensation pump which is connected between the rotary pump and the system reduces the pressure still further by pumping the gas from the system to the inlet of the oil pump where the definite backing or forepressure is maintained.

Condensation pumps can be divided into two classes. Mercury vapor is the pumping fluid in the one while the second uses the vapor of high boiling organic liquids. The mercury condensation pump is limited to a vacuum of 2.4×10^{-3} mm. mercury, the vapor pressure of mercury at room temperature, when it is used without a cold trap. If a cold trap with liquid air as refrigerant is used with the mercury condensation pump, vacua of 10^{-6} mm. of mercury can be obtained. Oil pumps have the advantage of being able to pump vacua up to 5×10^{-8} mm. of mercury without the use of cold traps. Vacua of 10^{-9} mm. of mercury are claimed when a cold trap is used with a good oil pump. Oil condensation pumps, in general, require a lower forepressure than do mercury condensation pumps.

*EDITOR'S NOTE.—The word "speed" in vacuum-pump terminology refers to *evacuation rate* in liters per second.—M. F. Behar

MERCURY CONDENSATION PUMPS

Two-stage Condensation Pump

A two-stage condensation pump based on original design of E. K. Kurth and modified by W. A. Ruggles⁵ is shown in Fig. 100. This pump is not difficult to make and is suitable for most small laboratory systems. The speed of the

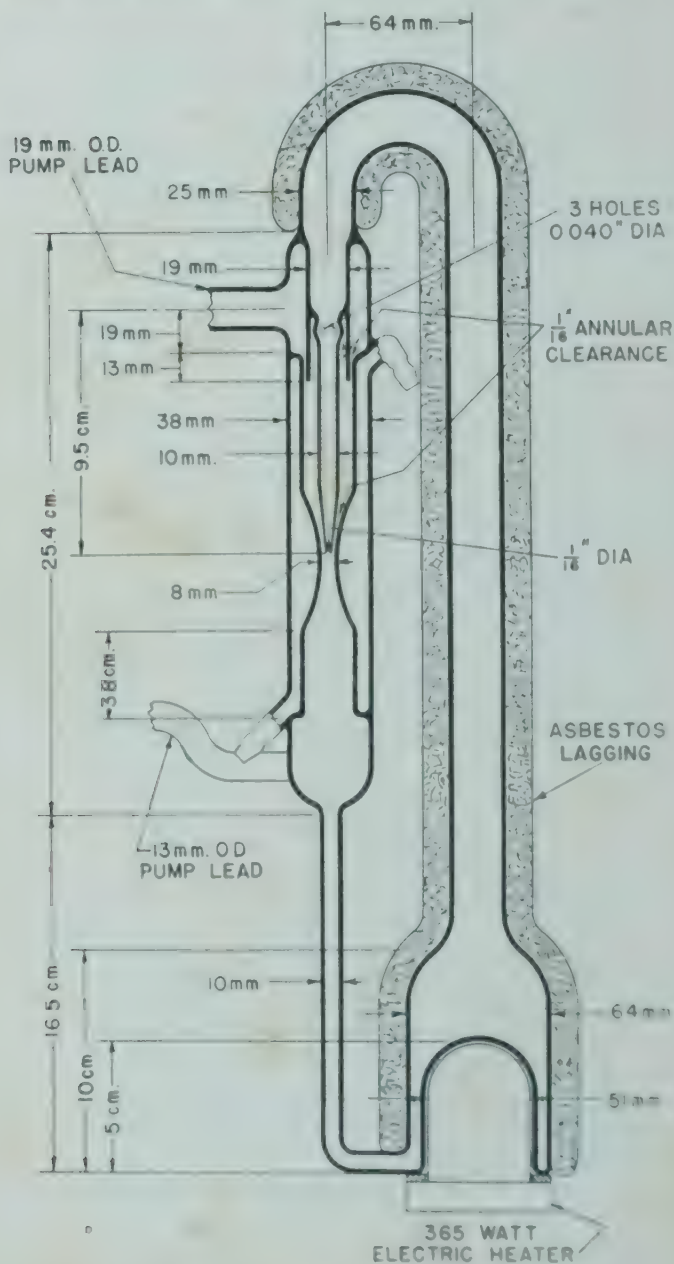


Fig. 101

pump is about 3 to 4 liters per second. It is fairly compact and can easily be installed. The critical dimensions are given on the assembly drawing Fig. 101 while the detailed parts are shown in Fig. 102. The recommended procedure for making the pump is as follows:

1. All parts must be made before the pump is assembled. Two rubber tube condenser side arms are made as described in Chapter III and illustrated in Fig. 42. Points are pulled on 15 cm. lengths of tubing with diameters of 25, 19, 13 and 10 mm. respectively. The tube ends are opened for sealing as illustrated in Fig. 27. These tubes are to be used respectively for the mercury vapor inlet, gas inlet, gas outlet and liquid mercury return. A 25-cm. length of 10-mm. diameter tubing is sealed to a 30-cm. length of 38-mm. tubing. This tube is to serve as the outer jacket of the pump. The inner jacket is made of 25-mm. tubing. The tube is constricted to the desired diameter as shown and flares are made on both ends. The flares should just fit into the 38-mm. tube. The inner jet is made by blowing a 13-mm. bulb in a 20-cm. section of 10-mm. tubing. The tube is cut 6 mm. above the bulb and the glass is flared to fit snugly into a 19-mm. tube. The small holes in the bulb are conveniently made with a pointed tungsten rod 0.04" in diameter mounted in a round Transite handle. The point of the rod is held against the bulb and the former is heated until red hot. This hot rod is rotated and pressed against the bulb until it pierces a hole in the wall of the bulb. One must be careful not to direct the burner flame against the bulb. Tungsten vaporizes under the intense heat of the burner flame and if it is directed toward the bulb, the vaporized tungsten will stain the glass. The tube is drawn down to a tip until the inside diameter is $\frac{1}{16}$ ". The length of the jet is 9.5 cm. The outer jet is made of 19-mm. tubing. A point is drawn on a 15-cm. length of this tubing and the end is opened in the burner flame and flared slightly. The tube is then cut with an abrasive wheel 5 cm. from the flared end. The inner jet is sealed into the outer jet as illustrated in Fig. 102A. The seal is then carefully annealed.

2. The pump is assembled by first sealing the inner jacket into the outer jacket. The bottom ring seal is made first; and the hose side arm connection and gas outlet tube are sealed to the outer jacket in respective order. The entire end is then annealed.

3. The top ring seal of the water condenser is completed after the bottom seal is cold; and the hose side arm connection is sealed to the outer jacket. The gas inlet tube is sealed to the outer jacket. The ring seal and side arms are then carefully annealed, Fig. 102B.

4. The jet assembly is inserted into the pump and the end is closed, Fig. 102C.

5. The pump is then inverted and the jet is centered in the water condenser. The flare on the outer jet tube is spotted to the outer jacket and the ring seal is completed by

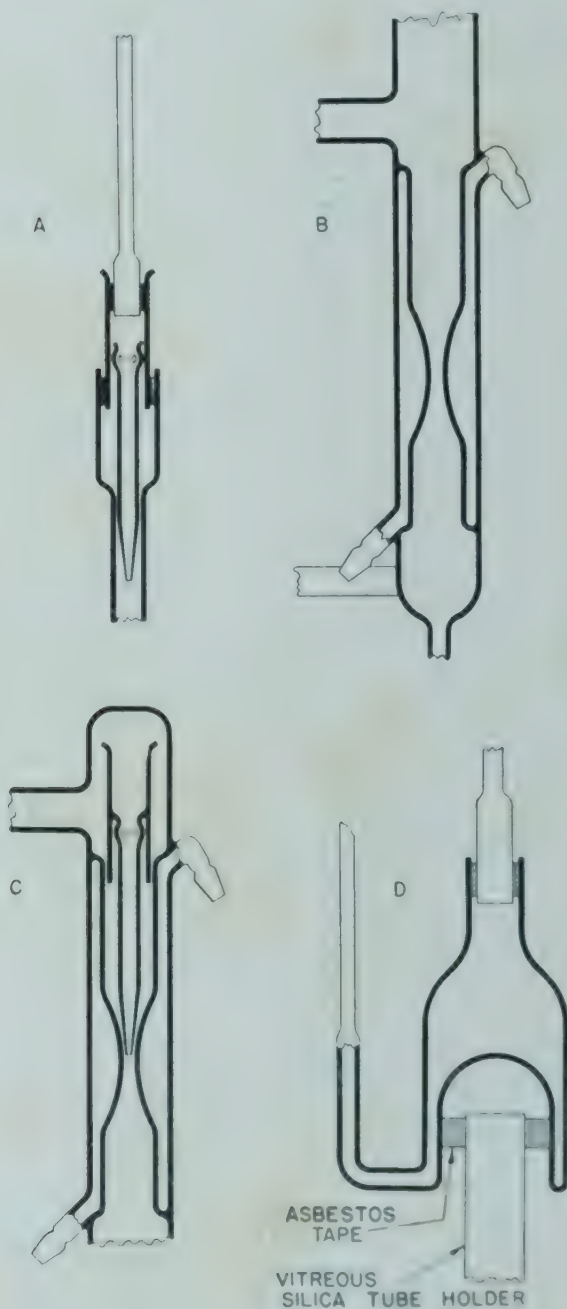


Fig. 102

fusing the glass against the flare of the jet, blowing out the glass and sealing the 1" tube to the jacket. The 1" tube is cut with the flame one inch from the ring seal. The seal is then carefully annealed.

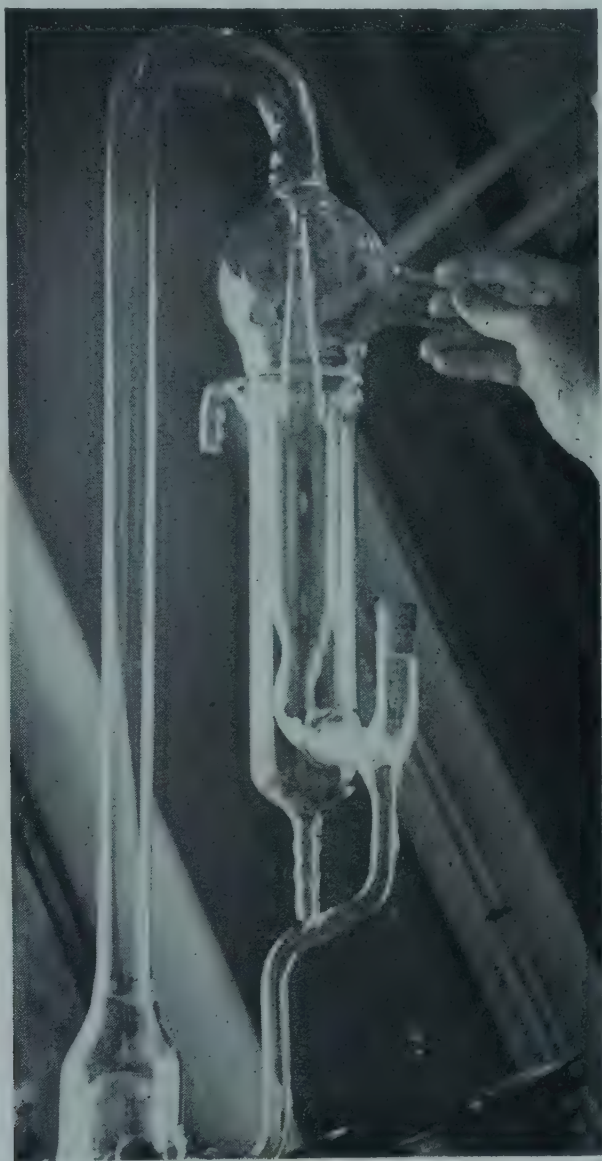


Fig. 103

6. The boiler is made by making a flare seal between a 51-mm. and a 64-mm. tube. A point is drawn on a 15-cm. length of 51-mm. tubing and the opposite end is opened in the flame and then flared. The flare should fit over the end

of a 64-mm. tube. The flared tube is then mounted on a vitreous silica tube, with asbestos tape, and the tube is closed and shaped into a round bottom 5.5 cm. from the flare. A 25-mm. to 64-mm. tubing seal is then made and the latter is opened in the burner flame 10 cm. from the seal. The flare seal is then completed as illustrated in Fig. 102D. The seal is easily made by using a glass blower's lathe, but is not too difficult by hand. The mercury return side arm is sealed to the boiler. The entire boiler is then annealed.

7. The vapor tube and the mercury return line are then sealed to the pump with a hand torch. The two parts are conveniently clamped on a rack while the torch seals are completed.

A heater for the mercury boiler can be assembled from parts purchased from the Westinghouse Electric Corp. The heating element (212 watts, 110 volts) from the Westinghouse Meadville works and the ceramic base (bee-hive type porcelain blocks, Style 8517-A, EDSK 82240, Drawing No. 1321) from the Westinghouse Derry Works. (Write directly to Meadville, Penna. and to Derry, Penna. because these are not regular catalog items with which Westinghouse sales offices are familiar.) The heating element is covered with a thin layer of alundum cement and is adjusted in the dome of the boiler so that the heater does not contact the glass. The boiler and vapor tube to the top ring seal is covered with asbestos tape and lagging. The latter asbestos covering is applied after it is mixed with water and can be smoothed with a small trowel. Johns-Manville Company asbestos cement No. 352 is excellent for this purpose.

The mercury vapor from the boiler enters the jet assembly. A portion of this vapor passes through the three jet holes and downward through the annular opening, Fig. 101. Gas molecules from the inlet are swept along with the mercury vapor until the latter condenses on the water jacket. The remaining mercury vapor passes downward through the second jet and sweeps the gas molecules down to the lower section of the pump where they are removed by the rough pump which is connected at the outlet line. The mercury vapor from the second jet is condensed by the water jacket and returned to the boiler by gravity flow. This two-stage mercury condensation pump requires a forepressure of about 0.1 to 0.2 mm. of mercury. A good mechanical pump is required for producing this forepressure and to maintain a proper evacuation speed.

Divergent-nozzle Pumps

A divergent-nozzle pump which is useful as a laboratory instrument is shown in Fig. 103. A series of pumps with

various annular widths between the nozzle and condenser were first designed and tested by T. E. Phipps⁶ and co-workers. The long-divergent-nozzle pump was found more

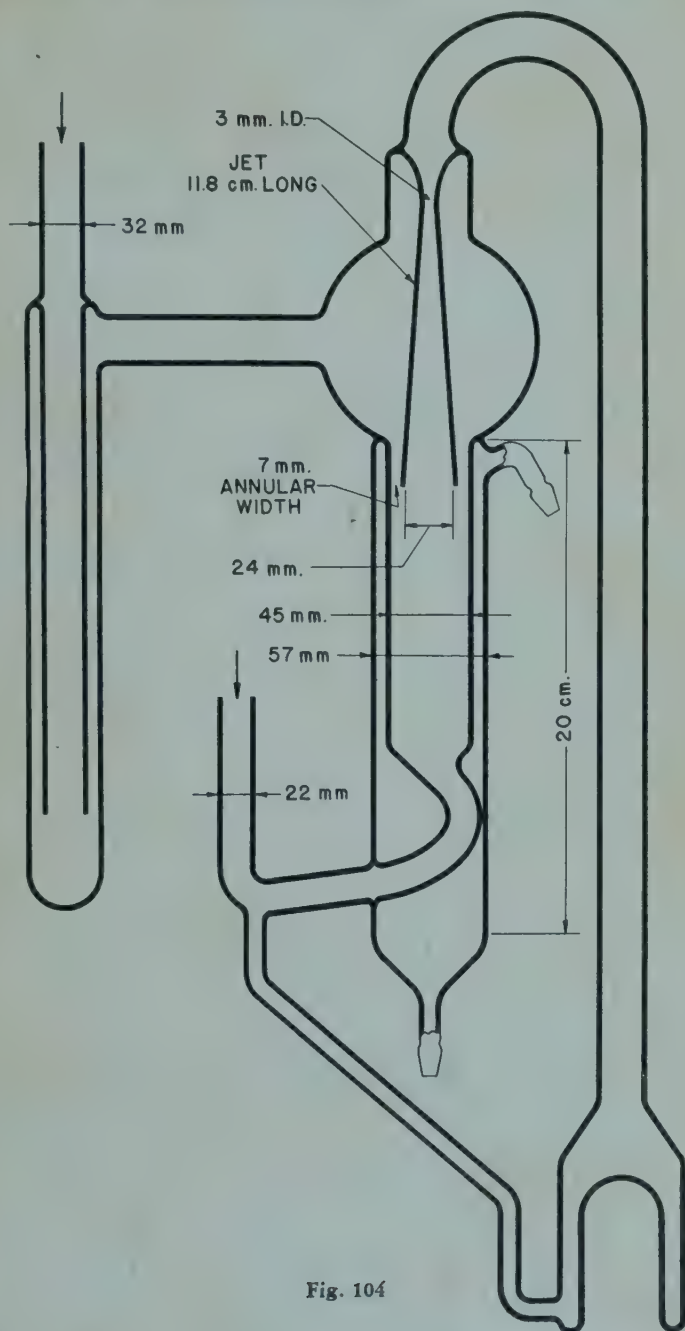


Fig. 104

efficient than pumps with short divergent nozzles. The critical dimensions of a pump which has a pumping speed of 5

liters per second when the forepressure is 0.003 mm. of mercury are given in Fig. 104.

The fabrication of the pump is quite simple. All parts should be made before it is assembled.

1. The divergent nozzle is made by gathering glass on a 28-mm. O.D. tube. The glass in this section is then drawn down until a smooth nozzle is formed. The glass beyond the apex of the cone is cut open and flared to fit the tube connected to the bulb. The jet is then cut from the tubing with an abrasive wheel.

2. The jacket contains a goose neck for more efficient condensation of mercury vapor. The inner jacket is made by pulling a point on a 45-mm. tube. The end of the tube is then flared to fit into the outer jacket which is 57 mm. in diameter. The tube is then mounted on a tube holder at the open flared end and a 22-mm. tube is then bent as illustrated and cut so that the end of the tube touches the outer jacket when the 45-mm. tube is parallel to the outer jacket.

3. Two hose connections are made for the water inlet and outlets.

4. A point is drawn on each of two 13-cm. lengths of 28-mm. tubing. The tube ends are opened with the burner flame. The glass bulb is conveniently made from a 300-ml. round-bottom flask. The inside diameter of the neck of the flask must conform to the diameter of the nozzle flare. The flask is opened directly opposite the neck. This opening should be about 57 mm. in diameter so that it can be sealed to the jacket.

5. The pump is assembled by first making the large ring seal at the top of the condenser. The inner jacket must be held rigidly in place so that the large ring seal can be made. Asbestos tape is a good filler for most mounting purposes but in this case it has the disadvantage of being too weak. Two pads must be placed between the inner and outer jackets. A length of tape from each pad will permit one to draw out the pads after the seal is completed. Since asbestos tape which has its filler removed by burning is not strong enough, it has been found advantageous to use a glass fiber tape. This tape must be cleaned by soaking it in an acid cleaning solution, washing with water and finally drying it at 300°C. Two pieces of this tape are folded into 3" pads with a streamer about one foot long on each. The pads are wedged between the inner and outer jackets while the streamers extend to the open end of the tube. This end is mounted on a holder. The top ring seal is then made by fusing the glass of the outer jacket against the flare and working the glass by blowing it out and tooling it with a flat carbon tool. The glass is cut in the burner flame 3 mm. beyond the ring seal.

6. The large opening in the flask is immediately sealed to the outer jacket. The ring seal and bulb are kept hot while this operation is being performed.

7. The gas inlet tube is sealed to the bulb and the bulb and ring seal are carefully annealed.

8. The nozzle is then inserted into the neck until the bottom extends 10 mm. into the water condenser. The nozzle is held in place with a thin carbon rod and the flare and glass of the neck are spotted in three spots. The ring seal is then completed and a short section of 28-mm. tubing is sealed to the glass above the ring seal. The nozzle must be centered after the ring seal is completed. This seal is then annealed.

9. The side ring seal on the side jacket is then completed after the glass pads are carefully removed. When this ring seal is made the entire tube end should be heated.

10. The end of the outer jacket is then drawn down and the hose connection is sealed to the reduced end of the jacket. The entire end is carefully annealed.

11. The mercury-boiler mercury vapor line and mercury return line are made as previously described and illustrated in Fig. 102D. The outer jacket of the mercury-vapor trap is made from 45-mm. tubing while 32-mm. tubing is used for the inner tube and gas inlet sidearm.

Combination

A combination of the two-stage pump, Fig. 100, and the divergent-nozzle pump, Fig. 103, is quite useful for a vacuum system. The double jet pump is used between a rotary oil pump and the divergent-nozzle pump. The forepressure for the latter pump is thus reduced to a value at which the divergent-nozzle pump will function more efficiently.

SINGLE-JET MERCURY VAPOR PUMPS

A small single-jet mercury vapor pump is illustrated in Fig. 105. For convenience in building the pump, the respective fabricated parts are shown in Fig. 106. The pump is assembled as follows:

1. The inner condenser jacket, part B, is put into part A and the flare of the inverted seal is sealed to the wide end of part A. The tube extending beyond the flare seal is then fused and a round bulb is blown. The flare seal is kept hot while the bulb is blown. The tube is then opened at the top of the bulb and a small flare is retained around the opening so that a ring seal can be made between the bulb and the outer edge of the shoulder of part C. This ring seal is made and tube D is sealed to the jacket at the flare seal. Tube E is then sealed to the bulb. The entire end of the pump is then carefully annealed. After the pump has cooled, the bottom ring seal is made and the side tube D is sealed to the water jacket. The gas outlet tube F is sealed below the

Technical drawing of a mechanical part, showing two views: a side view (left) and a top view (right).

Dimensions:

- Top view (right):
 - Overall width: 57 mm.
 - Distance from top edge to centerline: 25 mm.
 - Distance from centerline to right edge: 25 mm.
 - Distance from top edge to first bend: 83 cm.
 - Distance from first bend to second bend: 12 cm.
 - Overall length: 273 cm.
- Side view (left):
 - Overall height: 51 mm.
 - Distance from bottom edge to centerline: 25 mm.
 - Distance from centerline to left edge: 25 mm.

Labels:

- A: Top edge of the main body.
- B: First bend in the top view.
- C: Second bend in the top view.
- D: Port on the side view.
- E: Port on the top view.
- F: Port on the side view.
- G: Port on the top view.

Angles:

- Angle of the side view: 20° .

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A single-jet mercury vapor pump designed by J. E. Shrader and R. G. Sherwood⁷ is illustrated in Fig. 107. This pump is simple in design and can readily be made by anyone who has mastered the ring, flare and side-arm seals. The parts for the pump are first fabricated according to the dimensions given in Fig. 108. The pump is assembled as follows:

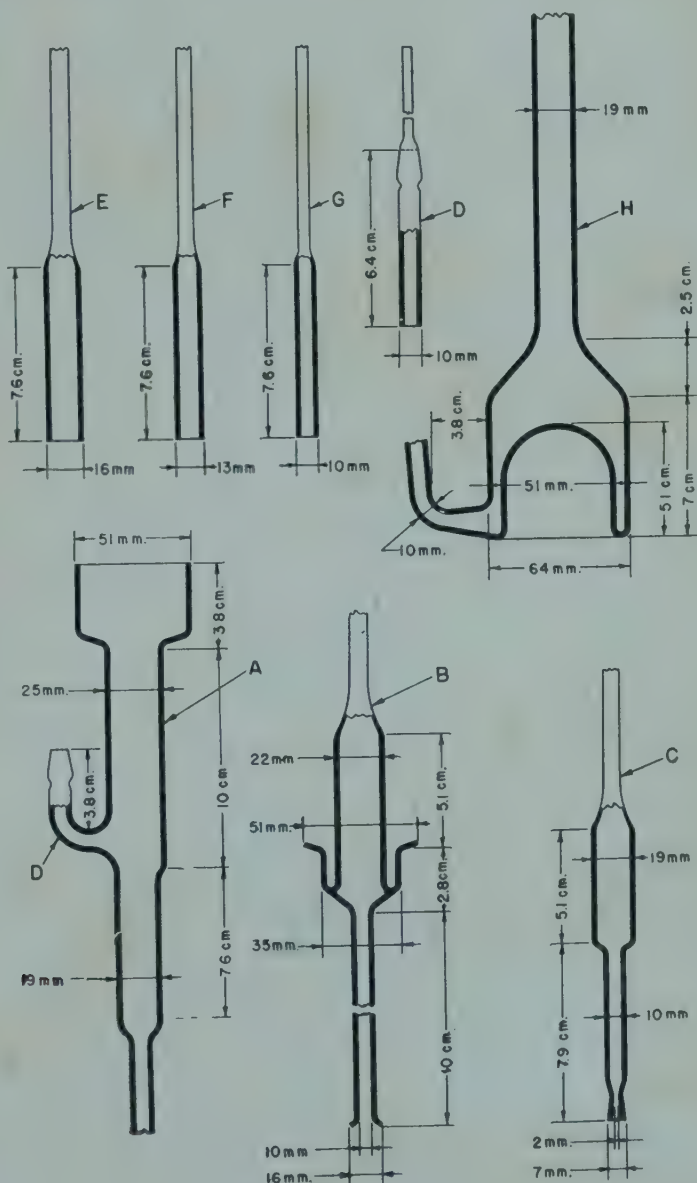


Fig. 106

1. Part B is inserted into part A so that the flare on the latter rests on the shoulder of part B. The glass of the flare and shoulder is sealed and a shoulder is blown below the seal in the glass of part A. The tube below the shoulder is opened with the burner flame and part C inserted into the opening until the shoulder of this part rests against the edge of the opened tube part B. The end of part C should

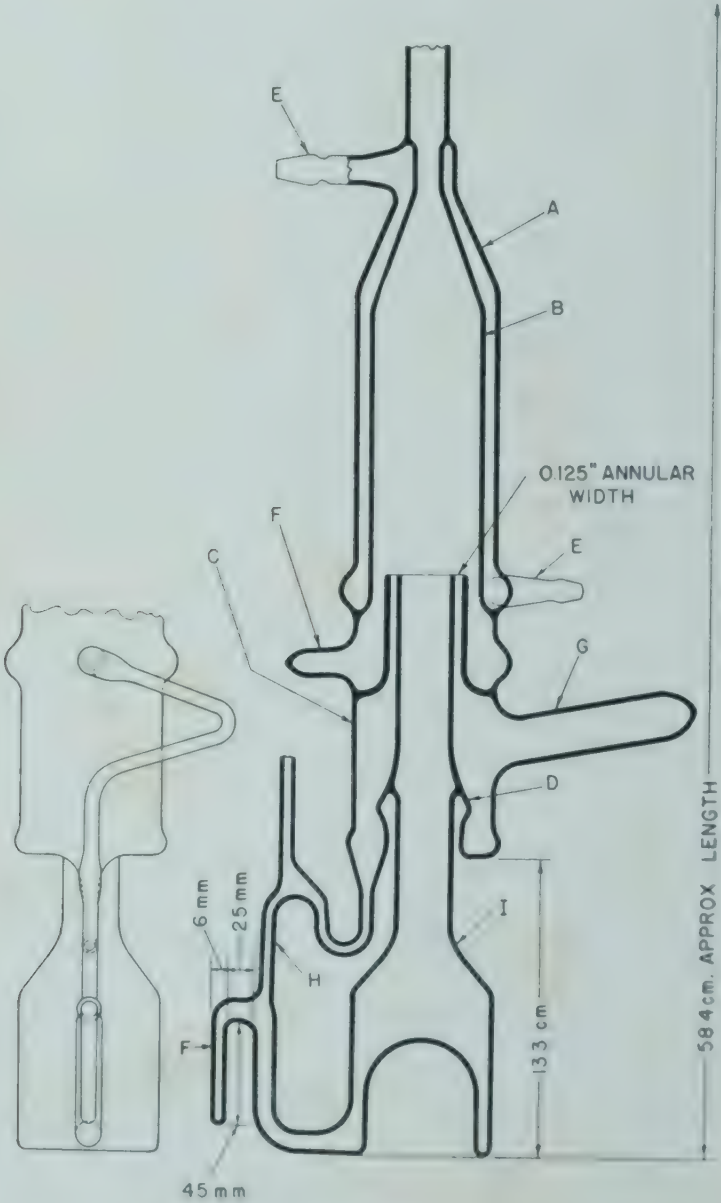


Fig. 107

extend 25 cm. into the water jacket. The glass at the juncture of part B and C is then sealed. A shoulder is then blown in part C just below the ring seal and the glass is opened below the shoulder. It is important that the glass be opened at exactly 13.3 cm. below the outer jet of part C. The inner jet, part D, with the inverted ring seal is then inserted into the opening until the flare rests against the open end. The flare seal is completed and the inner jet is centered in the pump. As the pump is being assembled as described above, it is extremely important that every seal be kept hot until all side arms are connected. After each ring seal is completed, the preceding seals must be heated so that no preheating will be necessary for making the side-arm seals. The side arms, parts E, F, G and H, are then sealed to the pump in this order. The entire section is then carefully annealed and allowed to cool slowly. After it is cool, the top ring seal is made and the side-arm hose connection, E, is sealed to the outer jacket of the condenser. The end is then annealed. The boiler, I, is sealed to the vapor line. The mercury return lines are sealed to the side arms of the pump and boiler.

A combination of the single-jet and the upright jet pump has been used by one of the authors for evacuation of vacuum jackets. The inlet of the single-jet pump is connected to the outlet of the upright jet pump. A rotary pump is used for producing a forepressure for the single jet pump. In trial runs it has been found that a forepressure as high as 2 mm. was sufficient to give a pressure of 10^{-5} mm. mercury on the high vacuum side of the upright jet pump. With a good backing pump, the combination will produce vacua of the order of 10^{-6} mm. of mercury.

ANNULAR JET PUMP

The recommended procedure for preventing the diffusion of mercury vapor into the system which is being evacuated is to use a trap which is surrounded by a refrigerant as liquid air. The conventional traps as illustrated in Fig. 119 are quite efficient in trapping the mercury vapor, but they reduce the effective speed of the condensation pump. Two alternatives are apparent for reducing the back diffusion of mercury vapor:

1. The amount of mercury vapor which diffuses back into the vacuum system can be reduced by more efficient water condensers in the condensation pump.
2. The speed of the condensation pump can be maintained by the use of traps which offer less obstruction to the flow of gases being pumped from a system and yet condense all mercury vapors.

An annular jet pump designed by C. S. Bull and O. Klemperer⁸ is shown in Fig. 109. The mercury vapor produced in a conventional boiler enters the pump jet through a large vapor line. The jet is annular to offer the least resistance to the gas which passes down into the mercury

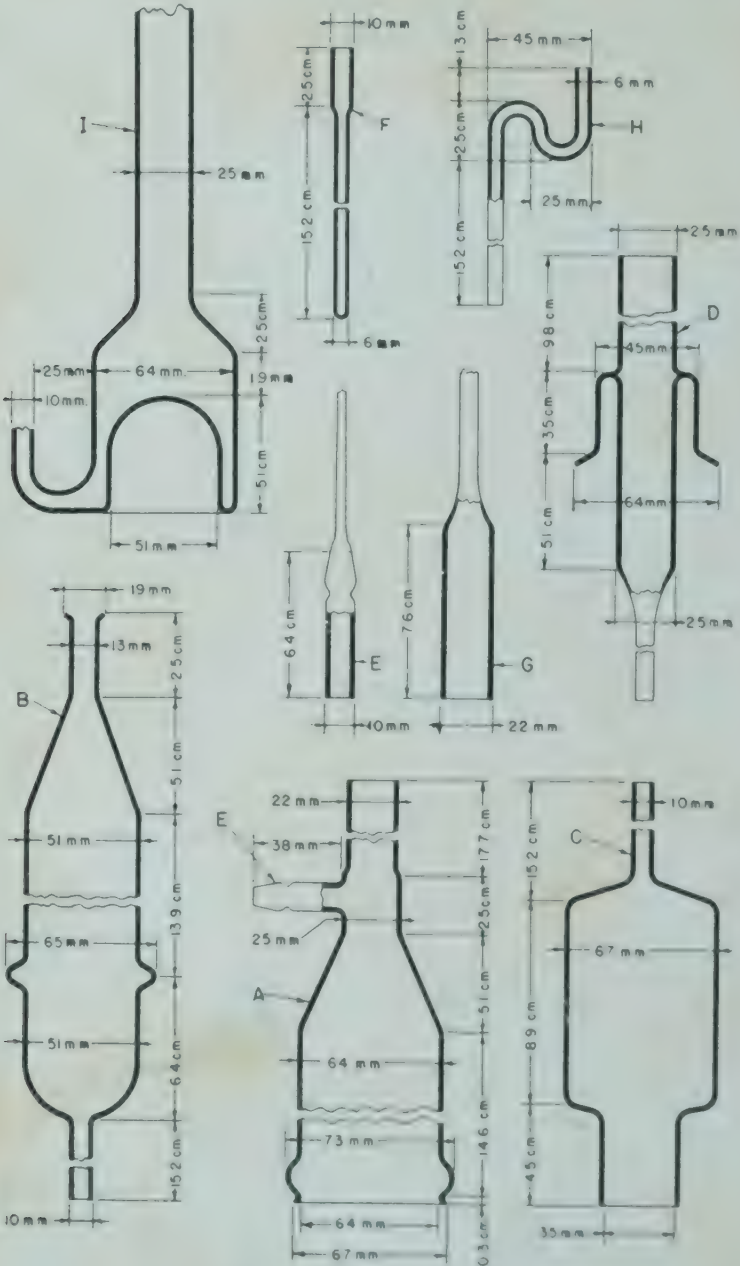


Fig. 108

vapor stream. An inner condenser and an outer condenser give a maximum of condensing surface. The condensed mercury returns to the boiler under gravity flow. The pump assembly has two additional features:

1. A trap is so designed that mercury vapor which diffuses back toward the vacuum system must impinge on a cold surface. The trap can be fabricated from glass or metal which does not amalgamate. Liquid air is kept in the trap and if the cone and baffle are made of metal, this assembly is made to give a close fit in the inverted glass seal which is part of the trap.

2. A metal shutter, which is closed to prevent migration of mercury into a vacuum system when the pump is not in use, is conveniently installed above the trap. The metal surface rests on a glass groove which has been ground flat for close contact between the glass and metal. The shutter is closed by the arrangement illustrated in Fig. 109.

The assembly shown in Fig. 109 was used to measure the speed of the pump which was calculated from the dimensions of the capillary and the respective pressures in the reservoirs on the high and low pressure sides of the pump. The speed of the pump was 90 liters per second at a pressure of 5×10^{-5} and 20 liters per second at a pressure of 3×10^{-6} mm. mercury respectively.

METAL NOZZLE MERCURY CONDENSATION PUMP

A mercury condensation pump with a metal nozzle was designed and tested by Estermann and Byck¹⁰. The pump details are shown in Fig. 110A and the nozzle details are given in Fig. 110B. The nozzle was made so that various annular areas could be tested by successively machining the inner and outer metal sections of the nozzle. The nozzle was made to give a friction fit over the glass vapor line from the boiler. The pump is simple in design and is made as follows:

1. A 50-mm. tube is flared at both ends. The overall length of this flared tube is 35 cm. The flares should fit into a 70-mm. tube. A 45-cm. section of this tube will be sufficient for the outer jacket. The end of the tubing which contains a size 50 inner member of a ground glass joint is opened for sealing to the reduced section of the outer jacket. Two hose connection side arms are made and a point is drawn on a 30-mm. and a 20-mm. tube, each of which is 15 cm. long. A mercury boiler is made as previously described. The vapor tube of the boiler is 15-mm. tubing. A small shoulder is blown 27 cm. from one end of a 37-cm. length of 15-mm. tubing.

2. The inner jacket is inserted into the outer jacket and one ring seal is made by fusing and working the glass of

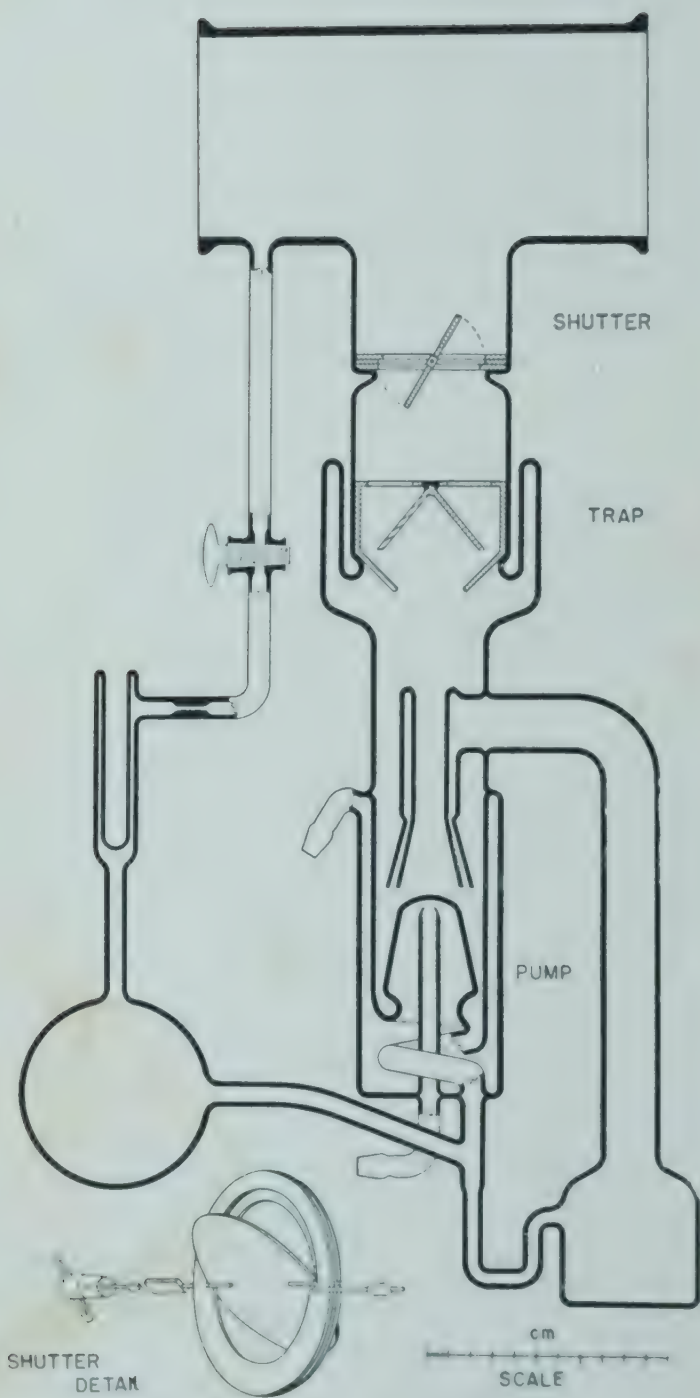


Fig. 109

the outer tube and the flare of the inner tube. The outer jacket is drawn down to the diameter of the tube containing the ground joint. This tube is sealed to the reduced section of the outer jacket and the side arm hose connection is sealed to the outer jacket. The end is then annealed and allowed to cool.

3. The bottom ring seal of the water condenser is then made and the hose connection is sealed to the outer jacket. The tubing below the ring seal is drawn down to 30 mm., opened, and a 30-mm. tube is sealed to the opening and the seals are annealed. The 30-mm. tube is opened to fit the

TABLE 15
PERFORMANCE OF METAL NOZZLE PUMP AT VARIOUS
CLEARANCES AND DIFFUSION AREAS

<i>Clearance in cm.</i>	<i>Area of Diffusion Region in cm.²</i>	<i>Pumping Speed of Air in liters per min.</i>
0.1	1.5	3.0
0.2	2.9	5.0
0.33	4.7	8.5
0.55	7.4	13.0
0.63	8.4	9.5
0.71	9.2	8.4

These tests were made by measuring the pressure at a point 30 cm. from the nozzle, which in practice, is the distance the vacuum system is located from the nozzle.

vapor tube shoulder. The vapor tube is ring-sealed and centered. The mercury return line and pump outlet are sealed to the pump in successive order and the entire end is annealed.

4. The boiler and mercury return lines are then sealed to the pump.

5. The Monel or stainless-steel nozzle is machined as shown and inserted into the pump through the top end. The nozzle tube should fit snugly over the glass vapor line.

Data of tests at various nozzle areas are given in Table 15; the pumping speeds at various clearances and diffusion areas are given in Fig. 111:

OIL CONDENSATION PUMPS

Condensation pumps designed for mercury cannot, in general, be used with oil. C. Burrows⁹ has given three main features in design which render mercury condensation pumps unsuitable for oil.

1. The clearance between the jet and condenser is too small, causing oil to bridge the gap when the pump is in operation.

2. The vapor lines leading to the jet have cross-sectional

areas which are not large enough to allow an adequate supply of vapor for efficient pumping.

3. The jet and vapor lines run too cool and cause condensation of oil vapor before it reaches the effective pumping area.

Oil condensation pumps must therefore be designed with a larger space between the jet and condenser. The minimum width is $\frac{3}{32}$ ". The vapor lines must be large and preferably short to permit adequate vapor flow and to prevent excessive condensation.

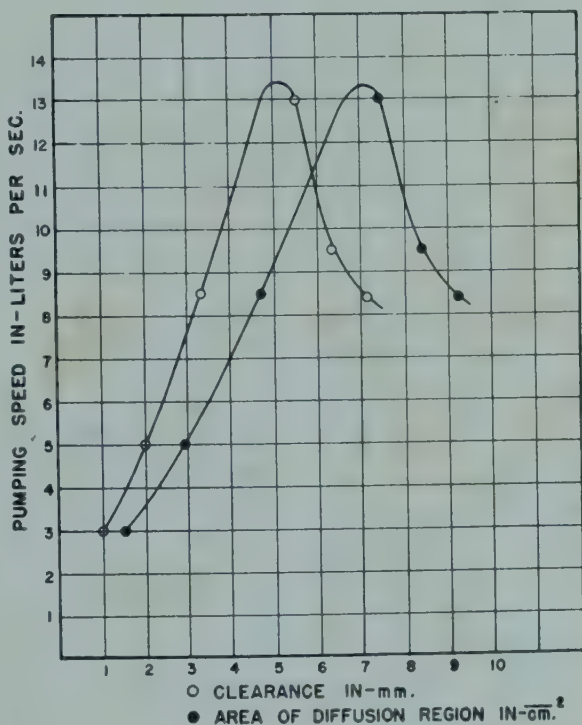


Fig. 111

Oils for condensation pumps can be readily obtained. Apiezon oils which are specific fractions of a petroleum oil were developed by C. R. Burch¹¹ and are supplied by the James G. Biddle Company, Philadelphia. Oils similar to Apiezon oils can also be obtained from the Litton Laboratories, Redwood City, Calif., and from the Central Scientific Company, Chicago. An extensive study of numerous organic compounds with high vapor pressures was made by Hickman and Sanford¹², who found that di-*n*-butyl phthalate and butyl benzyl phthalate were satisfactory. Octoil, which is superior to di-*n*-butyl phthalate was developed by Hickman¹³. The latter two oils, along with butyl sebacate

amiol, amoil S and Octoil S, are supplied by the Distillation Products, Inc., Rochester, N. Y.

Certain precautions must be observed in using oil condensation pumps. The oil must not be overheated because of the danger of decomposition. Overheating will result if the heat input to the oil boiler is too high, if the oil is not cooled sufficiently before it returns to the boiler, or if the

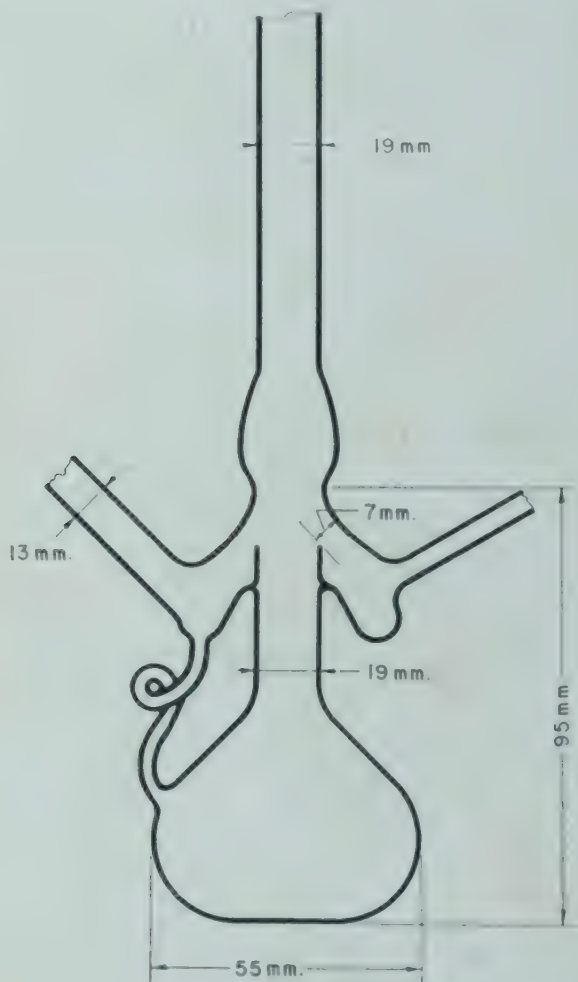


Fig. 112

backing pressure is too high. It has been found convenient to use electrical heaters on the oil boilers and it has been found that small coiled heaters which directly contact the oil are best from the standpoint of heat input. A boiler of this type is illustrated in Fig. 116B.

The assembly of glass oil condensation pumps will not be

given in detail because the techniques required have already been discussed in the preceding articles. Critical dimensions will be given and, if special assembly techniques are required, these will be described.

One of the early oil condensation pumps designed and tested by Hickman and Sanford¹¹ is illustrated in Fig. 112. The main assembly feature of the pump is the inverted ring seal. The boiler had a diameter of 55 mm. and the jet and outlet tubes were made of 19-mm. tubing. The high-vacuum inlet was made of 13-mm. tubing. A clearance of 7-mm. was allowed between the jet and condenser surface.

The speed of the pump which contained di-*n*-butyl phthalate was 6.5 liters per second when the condensing surface was not cooled by moving air. This speed was increased to 7 liters per second when the condensing surface was cooled with moving air. The watt inputs at the two speeds were 32 and 45 respectively. It was found that when copper wire was looped about the condensing surface, excellent thermal transfer was obtained.

Oil condensation pumps differ from mercury pumps in that permanent gases and vapor which are pumped are slightly soluble in the pumping oil. If no provision is made to segregate the lower-boiling, contaminating liquids or products of decomposition of the pumping oil, the pumping efficiency of the pump decreases. The pump shown in Fig. 113 is designed to make use of the fractionating principle for eliminating the contaminating materials from the last stages on the high vacuum side of the pump. This pump is supplied by Distillation Products, Inc., Rochester, N. Y. The physical and operation data of this pump are given in Table 16.

TABLE 16

PHYSICAL AND OPERATION DATA FOR TYPE 6F25W
THREE-STAGE WATER-COOLED FRACTIONATING PUMP

High vacuum connection	27 mm. I.D., 30 mm. O.D.
Forepump connection	
Vertical	Sealed off
Horizontal	22 mm. I.D., 25 mm. O.D.
Height, inches	13
Length, inches	25
Width, inches	5
Construction	Pyrex Glass No. 774
Weight, oz. net	48
Amount of oil, gms.	200
Recommended oil	Octoil-S
Forepressure, mm. of mercury	0.10
Heater Power, watts	90-250
Heater Current, amperes	1.4-2.3
Heater Voltage, A.C. or D.C.	65-108
Speed, liters per second	25
Ultimate Vacuum, mm. of mercury at 25°C.	5×10^{-8}

The forepressure required for this pump at various heater inputs is given in the graph of speed versus forepressures in microns ($1 \text{ micron} = 0.001 \text{ mm. mercury}$), Fig. 114. For vacuum in the order of $10^{-6} \text{ mm. mercury}$, the forepressure



Fig. 113

must be not more than 30 microns with a heater input of 1.5 amperes.

Speed versus high vacuum at various heater inputs is given in the graph of Fig. 115. The speed is constant over a wide range of pressure. A vacuum up to $10^{-6} \text{ mm. mercury}$

can be obtained in a short time. The ultimate vacuum of 5×10^{-8} mm. mercury can be obtained when Octoil-S is used as a pumping fluid. No liquid air trap is necessary. It is desirable, however, to have some sort of baffle arrangement to prevent oil molecules from leaving the pump. A right-angle bend of the low pressure side of the pump, Fig. 113, is satisfactory for preventing oil escape.

The boilers of this pump illustrate a feature which has become quite popular for oil pumps. The heating coils which are immersed in oil (the oil level is preferably $\frac{1}{4}$ " above the top of the coils) give uniform heating with a minimum amount of oil. Large surface area allows sufficient vapor-

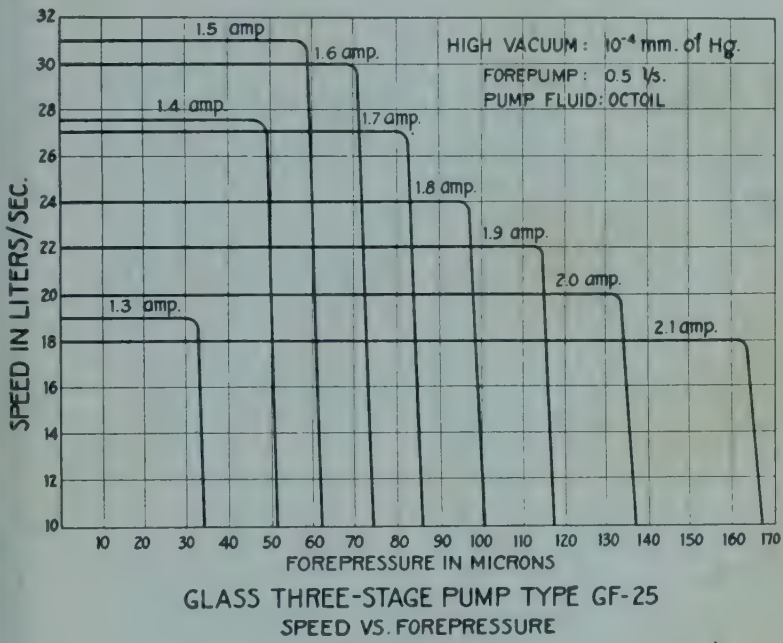


Fig. 114

ization area with a minimum amount of oil, thus reducing the amount of oil decomposition in each boiler.

A small oil condensation pump designed by C. H. Bachman¹⁴ is illustrated in Fig. 116. This pump was designed for a portable electron microscope and because of its size, can be used where small pumps are required. It can easily be set up in a 6" \times 6" \times 3" space. The pump is fitted with a ball-shaped baffle, and the tube leading to the backing pump is at a 7° angle to allow for oil drainage, should any get into the tube. A 3-mm. clearance between the beveled jet and condensing surface is recommended. The high-vacuum inlet is bent in two right angles to prevent back flow of vapor. The pump is charged with 35 cc. of oil. Each boiler is insulated to prevent heat fluctuations. The heater

on the high-vacuum side of the pump is made by coiling 0.018" nichrome wire, 78" long, on a $\frac{1}{8}$ " mandrel. The heater on the low-vacuum side is made of a 62" length of the same wire. The glass-to-metal seals can be made in many different ways. Four methods which have been used are the following:

1. A small Kovar cap with one hole in the bottom is sealed to the Pyrex Glass No. 774 boiler with a graded seal as described in the preceding chapter. The coil heater with two straight ends is then positioned in the boiler and the straight ends are passed through the holes in the Kovar cap. The heater wires are soft-soldered to the cap. Small

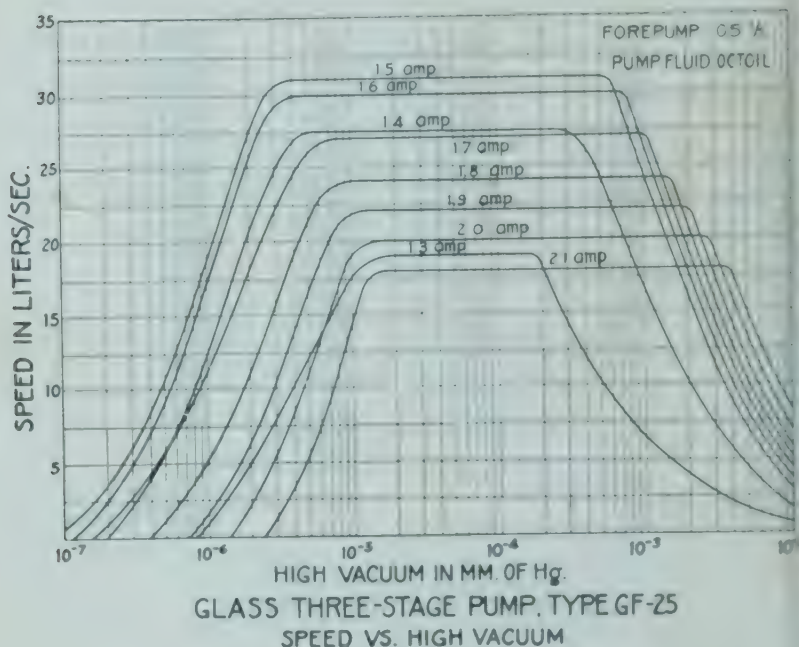


Fig. 115

clamps which snap over the caps can be soldered to the power lines.

2. Tungsten rods with copper braided wire on one end can be beaded and sealed into a flare. This flare is then sealed to the boiler through a graded seal after the heater coil is spot-welded to the tungsten rods. The Pyrex Glass No. 774-to-tungsten seal has been described.

3. It is sometimes convenient to seal the tungsten leads through glass by a glass press seal technique. Two wires can be sealed in one operation.

4. A tungsten rod is partly covered with a thin sleeve of 7051 glass. A Pyrex Glass No. 774 bead is made over a

part of the glass sleeve by fusing a thin rod to the sleeve and winding the fused rod on the sleeve until sufficient glass is collected for the bead. This bead is then sealed into the open end of the boiler side arm after the heater coil is spot welded to the tungsten rod.

The usual arrangement of the heater in the boiler is as

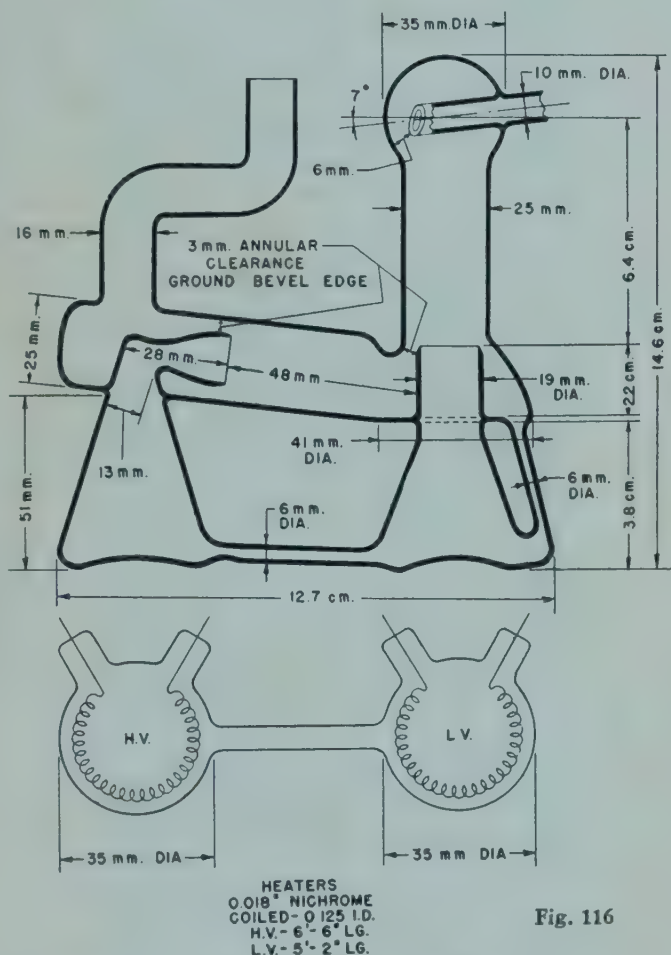


Fig. 116

illustrated in Fig. 116. If a two-wire glass press seal is used, only one boiler side arm is required.

An umbrella jet oil condensation pump designed by Estermann and Byck¹⁰ is shown in Fig. 117. The pump is shown with mercury seal ground Standard Taper joints. The detailed drawing of the pump is given in Fig. 118. The pump is assembled in a manner similar to the mercury pump previously described. The vapor line and umbrella jet, however, must be inserted through the top of the pump when the bottom ring seal is made.

The pump was tested with butyl phthalate and a pumping speed of 15 liters per second was obtained. The backing pressure required for this speed is 0.07 mm. mercury.

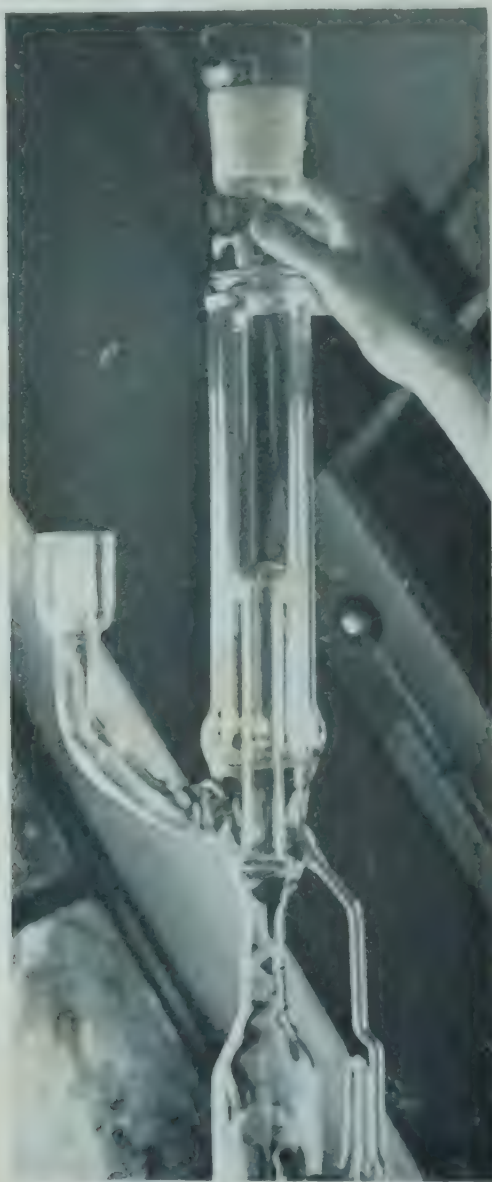
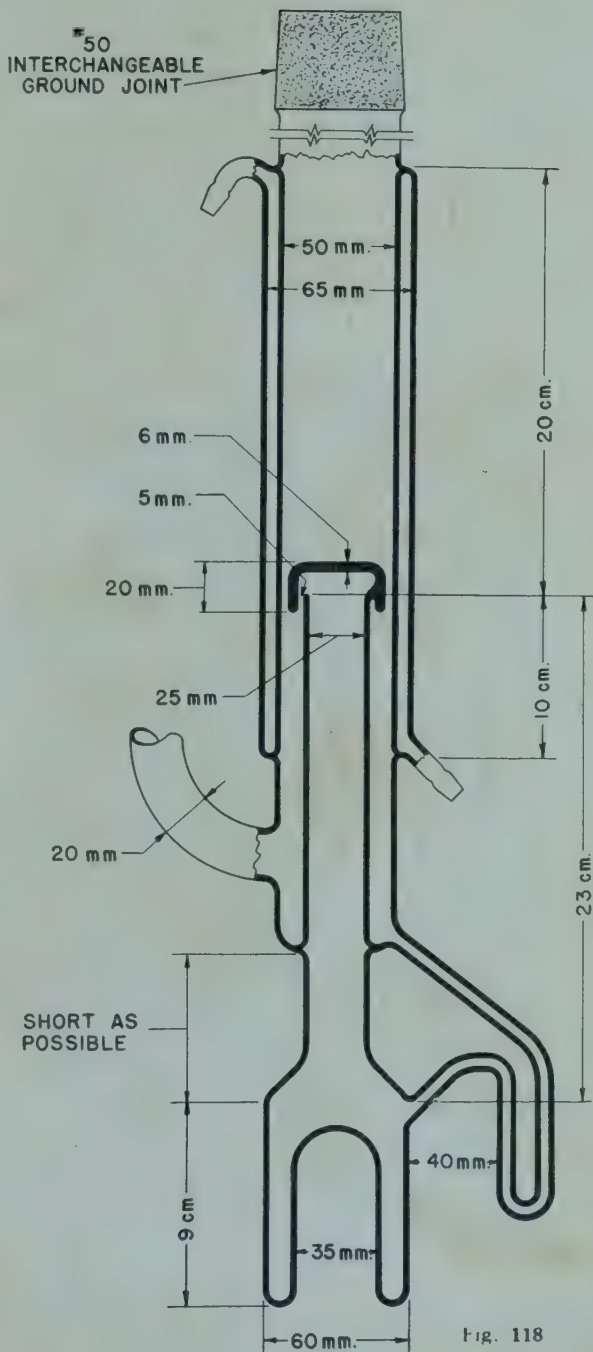


Fig. 117

TRAPS

Traps are necessary for preventing the migration of mercury vapor into evacuated systems when mercury condensation pumps are used. The trap design of Bull and Klemperer has already been discussed and the advantage of



this design, especially in a kinetic system, is that effective trapping is obtained without obstructing the gas flow from the high-vacuum system. However, the conventional traps, Fig. 119, still can be used quite effectively in small vacuum systems where speed of evacuation is not the prime requisite. The traps should be made with clearances in the order of 15 mm. The trap in Fig. 119A has a ground glass joint and should be used only when the trap must be cleaned frequently. The ground joint must be carefully lubricated. The conventional traps are illustrated in Fig. 119B and Fig. 119C. The latter is packed with granular activated charcoal, which, because of its absorptive properties, is quite

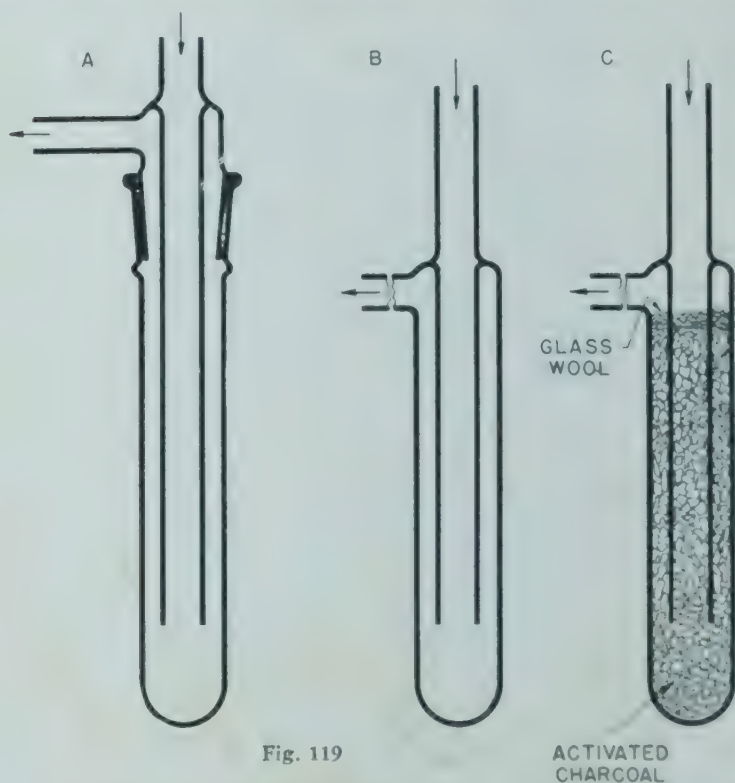


Fig. 119

useful for preventing mercury vapor diffusion, as well as absorption of residual gas. The charcoal can be reactivated by heating it to 800°C . while it is maintained under vacuum. The absorbing power of charcoal according to Dewar¹⁵ is given in Table 17.

The traps shown in Fig. 119 are immersed in a refrigerant contained in a Dewar flask to insure condensation of vapors. Liquid air is frequently used and, if the trap is in continuous use, it is desirable to have some means of supplying refrigerant to the trap Dewar. The vacuum-jacketed

TABLE 17

ABSORPTION CAPACITY OF COCONUT CHARCOAL

Volume of Gas at Standard Conditions of Temperature and Pressures per Unit Volume of Charcoal

<i>Gas</i>	<i>At 0° C.</i>	<i>At -185° C.</i>
Helium	2 volumes	15 volumes
Hydrogen	4 "	135 "
Argon	12 "	175 "
Nitrogen	15 "	155 "
Oxygen	18 "	230 "
Carbon Dioxide	21 "	190 "



Fig. 120

delivery tube shown in Fig. 120 is connected to a Dewar by a stopper. Air pressure applied to a blow line in the stopper forces the refrigerant through the delivery tube.

The delivery tube ring seals are made by the procedure outlined for simple straight-tube condensers. Only one side-arm tubulation is required on the outer jacket. The delivery tube is bent after the ring seals are completed by heating the outer tube at the desired point with a hot bushy flame until the outer and inner jackets are quite pliable. The glass is annealed and allowed to cool. The jacket is then silvered and evacuated.

Oil condensation pumps do not require elaborate traps when vacua up to 10^{-6} mm. mercury are required. Simple baffles or right angled bends in the high vacuum inlet of the pump have been successfully used. A trap designed by Hickman¹⁶ for use with oil condensation pumps is shown in Fig. 121. The trap is cooled with water and is quite effective in preventing back-diffusion of oil vapors.

MATCHING ROTARY VANE AND CONDENSATION PUMPS

Rotary vane oil pumps have definite pumping speeds at various pressures. It is necessary to know these speeds or the pumping characteristics over the pressure range which includes the backing pressure required by the condensation pump. In Fig. 99 the speed of the Welch Duo-Seal pump 1405 at 0.1 mm. mercury is 0.35 liters per second. If this

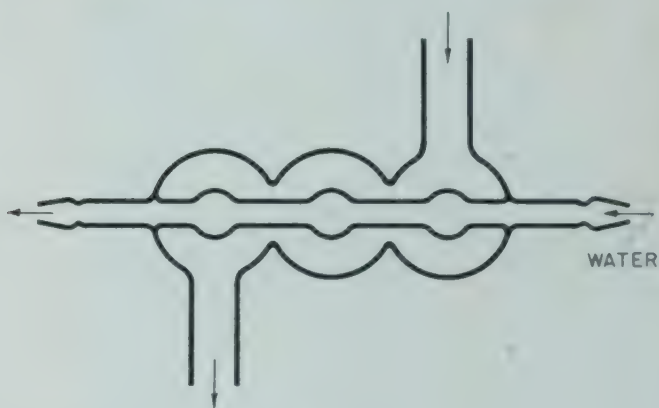


Fig. 121

pump is to be used with a condensation pump which requires a forepressure of 0.1 mm. mercury, the speed of the latter pump must not be greater than 0.35 liters per second when measured at the outlet side of the condensation pump. The speed on the high-vacuum side will be greater because of the lower pressure. As an example, suppose the condensation pump operates at a speed of 25 liters per second at 0.001 mm. mercury. This speed as measured on the outlet side of the pump is $(0.001 \times 25) 0.1$ or 0.25 liters per second.

The Welch Duo-Seal pump 1405 would be a satisfactory backing pump for the condensation pump cited in the above example, for under the pressure conditions, this rotary vane oil pump is capable of pumping 0.35 liters per second. However, if the Welch Duo-Seal pump 1400 is used, which under these pressure conditions pumps 0.175 liters per second, the

speed of the condensation pump is reduced because the backing pump is not able to move the gas fast enough.

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CHAPTER X.

VACUUM GAGES

Numerous gages for measuring various degrees of vacuum have been developed, but no single gage has been found which can be classed as a universal practical gage over the entire range of low pressures. Each has some distinct disadvantage, either in construction details or auxiliary equipment which must be used with the gage. Usually it is best to adopt the gage which is most suited for the particular pressures required. It is sometimes necessary to use several gages on a single system. Each gage can then be used in its recommended range and with such a combination it is possible to attain greater accuracy in pressure measurements.

Vacuum gages can be divided into two types or classes. The first type operates on the principle of comparing the unknown pressure with a known pressure by the difference in liquid levels or by a type of Bourdon tube which is deflected from the null point by the pressure within the tube. The second class depends on the number of gas molecules present in the gage and their respective properties.

SIMPLE MANOMETERS

The simplest vacuum or pressure gage is the manometer which consists of a U-shaped tube containing a liquid of known density and so arranged that the difference in level of the liquid may be observed. The space above the liquid on one side may be evacuated or exposed to a chamber containing gas at a known pressure. The pressure in the system attached to the other side of the manometer is then read as being greater or less than the known pressure on the other side, by a pressure equivalent to the difference in height of the liquid in both legs. A closed-end manometer is useful when pressures in the range of 1 to 20 mm. of mercury are to be read. They occupy little space and use small amount of mercury. In almost all cases a constriction in the tubing at the manometer bend is necessary for preventing rapid liquid surges when the pressure on one side is suddenly changed.

While in principle the manometer is very simple, there are certain principles which must be considered in its construction, especially if the manometer is used for accurate pressure readings. The rise or depression of liquids in small bore tubes is given by the following equation:

$$h = \frac{\gamma \, 2 \cos \theta}{r \, g \, d}$$

where γ =surface tension of liquid in dynes/cm.;
 r =radius of the tube in cm.;
 h =rise or depression of liquid in tube in cm.;
 g =acceleration due to gravity cm./sec.²;
 d =density of liquid in gm./cm.³;
 θ =angle of wetting of liquid with side wall.
 $\theta=0^\circ$ for complete wetting;
 $\theta=180^\circ$ for non-wetting.

Water and mercury can be considered as extreme cases of manometer liquids. Their respective surface tensions are 72 and 465 respectively at 20°C. Substituting these values in the above equation along with the proper density and gravity constants and assuming complete wetting of the surface in the case of water and complete non-wetting in the case of mercury, the capillary rise or depression for various tube radii given in Table 18 are obtained.

TABLE 18
EFFECT OF TUBE RADII ON CAPILLARY RISE

Radius of Tube mm.	Liquid Rise in mm.	
	Mercury	Water
1.0	-6.8	1.47
5.0	-1.36	0.29
10.0	-0.68	0.15
20.0	-0.34	0.08

The negative values in Table 18 designate a depression. The manometer must therefore be constructed of tubing with uniform diameter. If the two legs are of unequal diameters, not only will there be a difference in height due to pressure but also due to capillary effects.

The angle of wetting is another factor which must be considered. In the calculation of the data given in Table 18, it was assumed that the wetting angle of mercury and water was 180° and 0° respectively. Fortunately in most cases this is not true and therefore the capillary effects are less by the factor, cosine θ . Even if both sides of the manometer are the same diameter, there can be a difference in the angle of wetting in the two legs caused by moisture or dirt on the surface of the glass. This will give a difference in zero point in the two manometer tubes. To minimize this effect the manometer tubing should be as large as possible. Tubing with diameters of 12 to 15 mm. is recommended when differences of ± 0.1 mm. of mercury are to be read.

For measuring pressures, the manometer is limited only by the strength of the confining glass tubes. For vacuum measurements, it is limited by the operator's ability to accurately measure the difference in height between liquid levels. For most mercury manometers even with level-reading instruments such as a cathetometer, pressures below 2 mm. are subject to considerable uncertainty.

The construction of the short simple U-tube manometer is not difficult. A section of glass is thoroughly cleaned. A portion near the center of the tube section is fused and constricted by rotating it in the burner flame. The constricted section should not be over 1 cm. in length and the outside

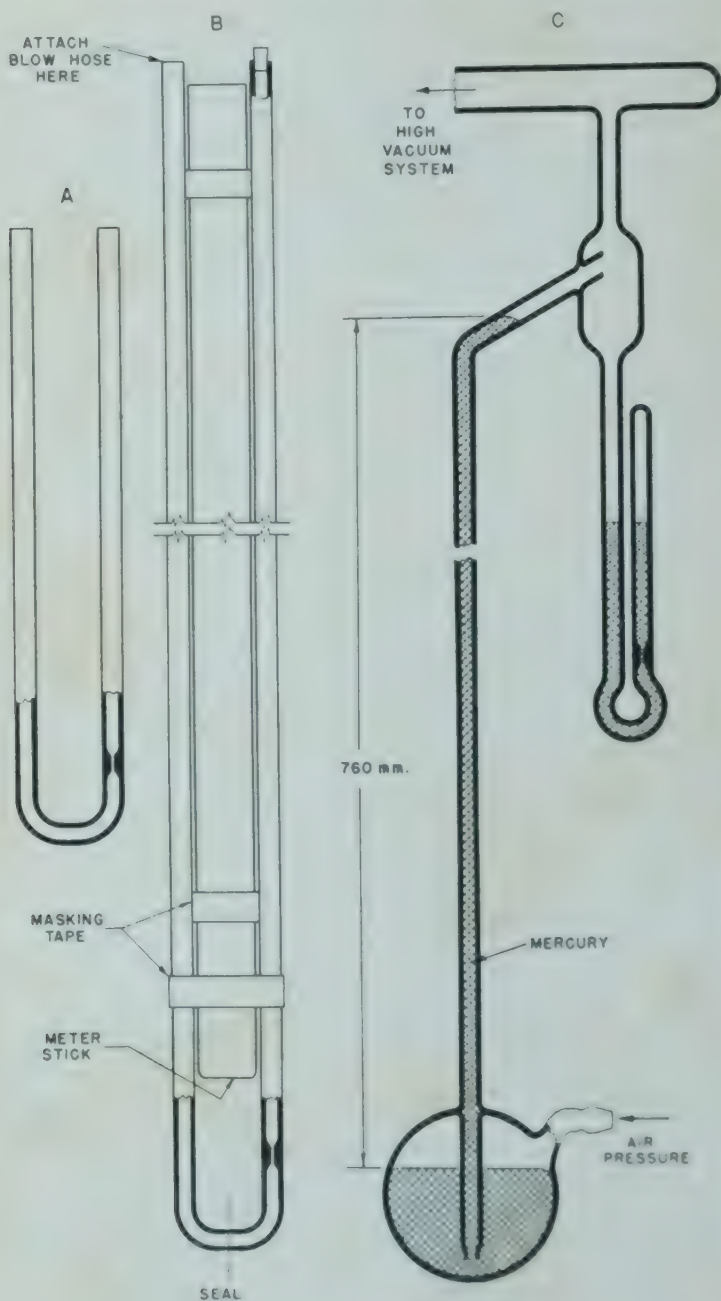


Fig. 122

diameter of the constricted section should be identical with the original tube. The glass tube is then bent into a U-shape as illustrated in Fig. 122A. The constriction in the manometer should be adjacent the bend. One leg of the manometer is closed.

Long U-tube manometers are convenient when a pressure range of 760 to 1 mm. of mercury is required. The fabrication of such manometers is not difficult if the two manometer arms are taped to a meter stick after the constriction and the tube ends are shaped as shown in Fig. 122B. The tubes are sealed together by fusing the ends of the two tubes. A blowing tube is fastened to the one open end while the other is stoppered.

Closed-end manometers are frequently used as approximate vacuum indicators in vacuum systems or for vacuum indicators where the accuracy of 10% is sufficient. These manometers usually are about 6" in length with the closed end completely evacuated. The production of these manometers is as described above. The manometers are filled with mercury by various methods. A practical method of filling several at one time is illustrated in Fig. 122C. A mercury filling tube 760mm. in length is ring-sealed into a large mercury reservoir. The opposite end is ring-sealed into a small bulb. Two outlets of the bulb are sealed to the open end of the manometer and the manifold of the vacuum system. Triple-distilled mercury is poured into the clean reservoir. The vacuum pumps are started and after a vacuum of the order of 10^{-6} mm. of mercury is obtained, the manometer is heated with a torch. After the manometer is properly degassed and a vacuum better than 10^{-6} mm. of mercury is obtained, the mercury in the reservoir is forced into the manometer by applying air pressure to the reservoir side tube. Several manometer filling units can be sealed to the same vacuum manifold.

MCLEOD GAGES

The McLeod¹ gage was among the first gages developed for measuring vacua and is still used extensively as a laboratory instrument. It is, in general, simple in construction and operation and, when properly calibrated, it is reliable within certain pressure ranges which will be discussed later. Moreover, gages can be made to read pressures as high as 50 and as low as 10^{-5} mm. of mercury.

The principle of the gage is that of compression of a known volume of gas at an unknown pressure to a smaller volume. The pressure at the smaller volume can be determined by difference in height of a mercury column. Assuming Boyle's law we can then calculate the original unknown pressure by the equation:

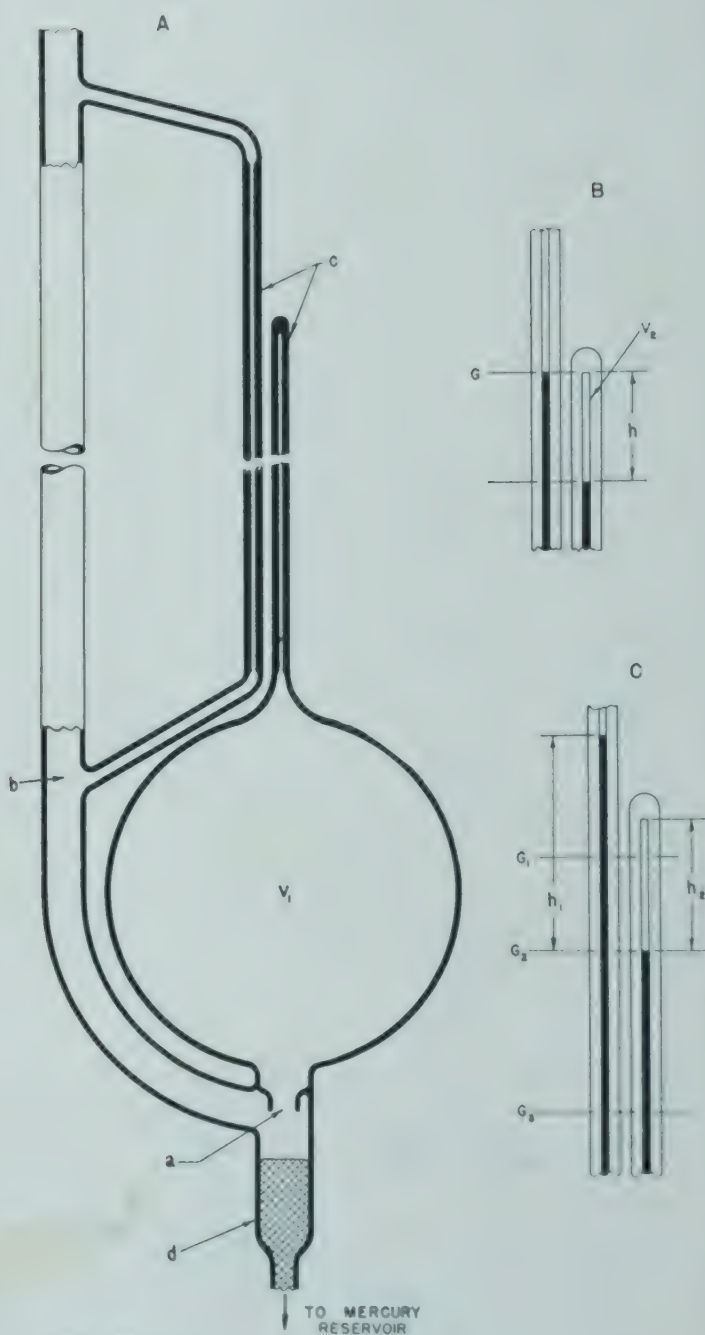


Fig. 123

$$P_1 = \frac{P_2 V_2}{V_1}$$

where P_1 = unknown pressure;

V_1 = initial volume before compression;

P_2 = final pressure;

V_2 = final compressed volume.

A simple McLeod gage is illustrated in Fig. 123A. It is operated by causing the mercury to rise and enter the bulb V_1 at a . The gas within the bulb and capillary c which is sealed to bulb V_1 is cut off from the rest of the system when the mercury passes through the ring at a . The gas in V_1 is compressed by the mercury until the mercury column in the outer capillary is coincident with the gage mark G which also coincides with the end of the closed capillary, Fig. 123B, or the mercury in the closed capillary becomes coincident with an arbitrary mark G as illustrated in Fig. 123C. In either case V_2 can be calculated from the length and radius of the capillary and P_2 is directly the height of the mercury column in the open capillary. V_1 is known and therefore the pressure P_1 can easily be calculated.

McLeod Gage Dimensions

For vacua in the range of 10^{-4} to 10^{-5} mm. of mercury, V_1 usually is 200 to 300 cc. in volume and the capillary diameter is approximately 0.5 mm. If a larger volume is used, the weight of mercury becomes excessive and an increase of several times V_1 gives little increase in gage sensitivity. However, if smaller capillary tubes, below 0.5 mm., are used, the mercury column separates when mercury is lowered in the gage. A gage with the dimensions given above has a sensitivity of $10^{-6} \times h^2$ mm. of mercury when read as illustrated in Fig. 123B. With a capillary 0.5 mm. in diameter and 200 mm. long pressures up to 0.04 mm. of mercury can be read. When higher pressures must be measured, 35 mm., a smaller ratio of V_1 and V_2 is required. A volume of V_1 of 8 cc. and a capillary 200 mm. long and 3 mm. in diameter will give measurements up to 35 mm. of mercury by the method illustrated in Fig. 123B. Pressures up to 50 mm. of mercury can be read on the gage by the method illustrated in Fig. 123C.

Calibration of McLeod Gages

The calibration of the McLeod gage may be either a simple or an elaborate operation depending on the subsequent use of the instrument. It should be pointed out that the accuracy of the McLeod gage is of the order of 1% even though a perfect calibration is made. Reasons for this percentage error when absolute pressures are measured will be discussed later.

The first step in calibrating parts of the gage is to choose several 60-cm. lengths of capillary tubing with approximately the correct bore. These capillary tubes are carefully cleaned and dried. A small amount of clean mercury is drawn up into the capillary tube and the length of this section of mercury is measured as accurately as possible. The length and position of the mercury are recorded. The thread is then moved to the adjacent portion of the capillary tube and the length and position are again recorded. This process is repeated, Fig. 124A, until the entire length of the

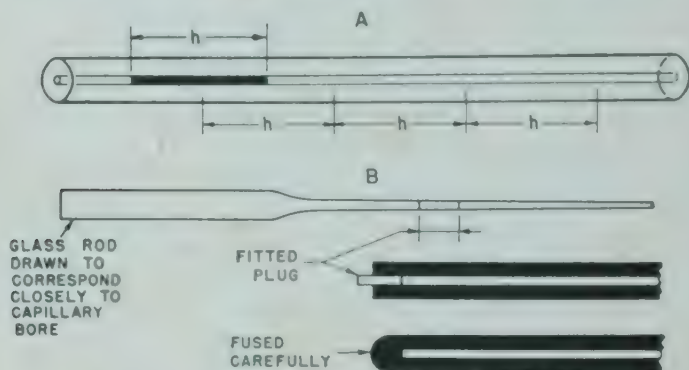


Fig. 124

tube has been covered. By this procedure the uniformity of the bore can be determined. A plot of mercury thread length versus position on the entire tube can be made for a graphical representation of bore uniformity. It usually is not difficult to find capillary tubes with less than 1% variation. The mercury is then carefully removed and weighed on an analytical balance. By knowing the temperature of the mercury during the measurements, weight and density, it is a simple operation to calculate the radius of the capillary or its volume per millimeter of length. Repeated calibrations with different thread lengths of mercury can be made if greater accuracy is required.

Two sections of capillary tubes are then chosen for the gage. One is closed by using the procedure illustrated in Fig. 124B. The capillary bore should be perfectly cylindrical to the end. The end is closed by first drawing a fused glass rod to a thin rod. A section of this rod with a diameter of the capillary is placed in the end of the capillary. The capillary tube is then heated at the end until the glass completely fuses. The tube section just below the end of the bore should not be deformed because of the danger of changing the volume of the capillary.

If the gage is to be used and read as illustrated in Fig. 123C, it is wise to determine the location of the gage marks

indicated by *G*. The capillary is first weighed and then is filled with mercury from the closed end to each respective mark and weighed. From the mercury density a direct calculation of the volume of the capillary from the marks to the closed end can be made. The volume per length as a function of length can be plotted and, as it takes into account any variations in bore dimensions, these data are preferred, particularly when the gage is to be read in this manner.

The capillary is sealed to the bulb V_1 , Fig. 123A, and the ring seal *a* at the bottom of the bulb is made as illustrated, Fig. 123A. The bulb V_1 is then filled with either mercury or water. The bulb must be filled exactly to the inverted seal or cut-off at *a*. No air pockets should be trapped in the bulb. If the calibrating liquid enters the capillary, a weight or volume correction can be made, by obtaining the volume of the particular section from the plot of volume versus position in the capillary. The amount of liquid in the bulb V_1 is then determined by weighing the liquid and with temperature measurements the volume can be obtained.

The gage is then assembled as shown in Fig. 123A. The capillary on the tube leading to the system should have a bore which conforms as near as possible to the closed capillary. A study of the graph of volume versus position of each capillary will aid in making the proper choice. One must be very careful that the volumes of the bulbs and capillary are not altered when the gage is made.

After the gage is assembled, it is mounted on a convenient rack or holder. A method of raising the mercury into the gage must be chosen. Two important factors must be considered. First, the flow must be controlled so that no rapid surge of mercury occurs as the mercury is raised, because of the danger of breaking the gage. Second, the flow must be controlled so that the mercury can be stopped exactly on the predetermined calibration mark on the gage.

There are several methods of raising mercury into the McLeod gage. Four commonly-used methods are as follows:

1. The simplest, although not necessarily the most satisfactory way of raising the mercury is by means of a mercury bulb and rubber tubing, as shown in Fig. 125A. This method is quite convenient but is not conducive to accurate setting of the mercury levels in the gage.

2. A second method is shown in Fig. 125B. In this case a full barometric leg is inserted between the cut-off of the gage and the mercury reservoir. It has its advantage in that the gage may be turned directly to the full vacuum line, thus eliminating any air that may be trapped. The barometric leg may serve also as an approximate indicator of the vacuum in the system. It has the disadvantages that

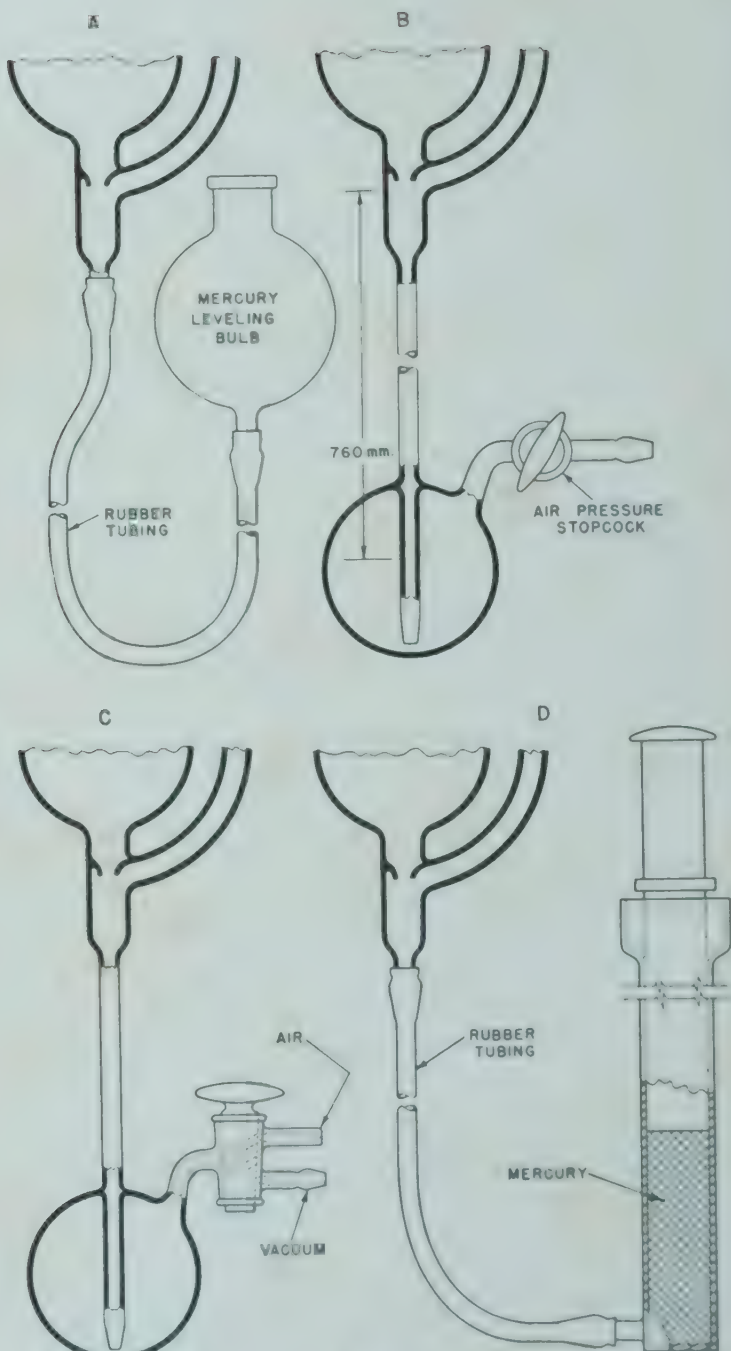


Fig. 125

the length of the gage is increased and that air pressure is required to raise the mercury into the gage.

3. The method shown in Fig. 125C is in general the most satisfactory for raising mercury into the gage. The mercury is raised by atmospheric pressure and returned to the reservoir by vacuum supplied by some auxiliary source. The rate of mercury rise can be carefully controlled by a three-way stopcock and capillary tube.

4. A method² by which the mercury is raised with a plunger is shown in Fig. 125D. This method is better than the first discussed above because it is quite simple to attach a simple ratchet or adjusting screw arrangement to control the mercury rise. The plunger and case are made of metal that will not amalgamate.

Methods of Reading the McLeod Gage

There are two methods of reading the McLeod gage. The first is illustrated in Fig. 123B. In this case the mercury in the open capillary is raised until it is just even with the end of the bore of the closed capillary tube. To get the pressure of the gas in the system one needs only to read the height and substitute in the following formula, which is derived by assuming the validity of Boyle's law:

$$P_1 = \frac{\pi r^2 h h}{V_1} \quad (3)$$

where V_1 = initial volume;

h = difference in height of mercury in the closed and open capillary;

$\pi r^2 h$ = final compressed volume

Equating

$$K = \frac{\pi r^2}{V_1}$$

we have

$$P_1 = K h^2 \quad (4)$$

A metric scale may be placed behind the two capillaries. The height is read directly and the pressure P_1 is then calculated for every reading. When only approximate pressure readings are required, a scale can be placed behind the capillaries which will allow one to read the pressure directly. This scale is prepared by calculating h for various unit pressures as 1, 2, 5 and 10×10^{-5} , 1, 2, 5, and 10×10^{-4} , etc. A scale of this type is illustrated in Fig. 126.

The second method of reading the gage is shown in Fig. 123C. Here the mercury is raised until it is even with some arbitrary gage mark G_2 . The pressure is then calculated as follows:

$$P_1 = \frac{\pi r^2 h_2 h_1}{V_1} \quad (5)$$

where h_1 = height of mercury in the side capillary;

h_2 = length of compressed gas in the closed capillary.

Since the same gage mark is used for a number of readings the formula can be changed to:

$$P_1 = K_2 h_1 \quad (6)$$

where

$$K_2 = \frac{\pi r^2 h_2}{V_1}$$

The original pressure P_1 is thus directly proportional to the height of mercury in the side arm. There is a definite advantage of reading a gage in this manner because a

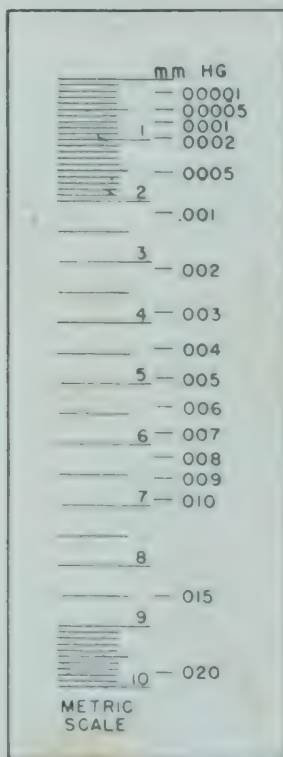


Fig. 126

number of gage marks may be used for various pressure ranges. The height of the gas column in the closed capillary h_2 can be so selected that the constant K_2 may be in some units of 10^{-2} . In other words the height of mercury in the outside tube need be multiplied by 10^{-3} or 10^{-2} , etc. to obtain P_1 directly.

The equations which have been discussed thus far are valid only for simple McLeod gages where P_1 is less than 0.1 mm. of mercury. If P_1 is not negligibly small, the equation for calculating pressure by the gage is:

$$P_1 = \frac{\pi r^2 h}{V_1} (h + P_1) \quad (7)$$

$$P_1 = K_3 h^2 + P_1 K_3 h \quad \text{where } K_3 = \frac{\pi r^2}{V_1}$$

Solving for P_1 we have

$$P_1 = \frac{K_3 h^2}{1 - K_3 h} \quad (8)$$

If gage marks as shown in Fig. 123C are used we have from equation (7)

$$P_1 = \frac{\pi r^2 h_2}{V_1} (h_1 + P_1). \quad (9)$$

Solving for P_1 we have

$$P_1 = \frac{K_4 h_1}{1 - K_4} \quad \text{where } K_4 = \frac{\pi r^2 h_2}{V_1}$$

$$\text{or } P_1 = K_5 h_1 \quad \text{where } K_5 = \frac{K_4}{1 - K_4}. \quad (10)$$

The scale which is calibrated for the quadratic equation (8) is the square scale while the scale for equation (10) is a linear scale.

When the McLeod gage is used to measure pressure above 0.1 mm. of mercury, another factor must be considered. The system quite often is small and when pressure measurements are made, the mercury in the large side arm appreciably compresses the gas in the system beyond the gage. The gage equation then becomes

$$P_1 = \frac{\pi r^2 h}{V_1} (h + X P_1) \quad (11)$$

where X is the compression factor which will depend on the size of the system and also the height to which the mercury is raised in the side arm. When the gage is read as illustrated in Fig. 123B, the final equation is

$$P_1 = \frac{h^2}{(V_1/\pi r^2) - Xh} \quad (12)$$

Equation (12) is quite complicated but it can be used. Moreover, X must be determined experimentally. The accuracy in determining this compression factor need not be extreme as $V_1/\pi r^2$ is usually a large number compared to Xh .

In order to surmount some of the difficulties discussed above, a different type of gage design is recommended. This gage is illustrated in Fig. 127A. The capillary side arm is completely separated from the system by means of an auxiliary side tube having a mercury cut-off. When the

mercury is raised in the gage and side arm, there is no external pressure equivalent to P_1 or XP_1 to be considered and the simple equations of $P_1 = Kh$ or $P_1 = K_2h^2$ can be used. The gage can be easily made and it is not difficult

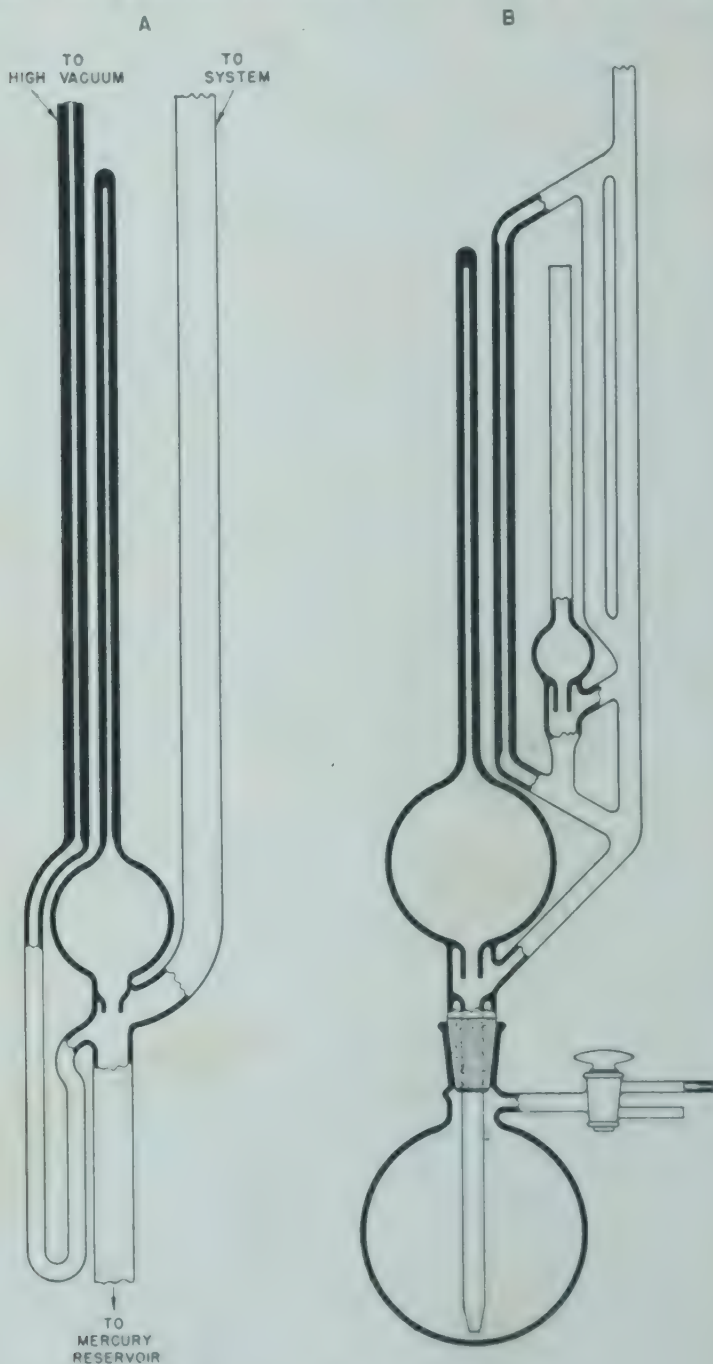


Fig. 127

to operate. It does have the disadvantage that it requires a separate line to the system. There is a little more added uncertainty in the wetting angles and capillary depressions for the gases in the gage proper may influence these factors. There should be no gases in the open-arm capillary.

McLeod Gage Installation

The gage should be cleaned and all dirt and liquids should be removed. The gage can be warmed with a small hand-torch flame and degassed under vacuum.

After the gage is mounted it is well to check the following:

1. When the mercury is raised in the gage which is subjected to a vacuum of 10^{-8} mm. of mercury the two levels in the capillary tubes should be the same when the mercury flow is stopped at various points below the closed end of the capillary. It may be necessary to tap the capillaries to overcome surface effects.

2. When the gage is read as shown in Fig. 123B, the pressure at each mark should be the same. This test is made at a pressure of about 10^{-3} mm. of mercury.

3. Measurements made on the same gas at the same pressure should all agree.

It has been pointed out in the discussion of manometers that capillary depressions are effective in a liquid such as mercury. It is therefore essential that the capillaries of the McLeod gage be tapped with the finger tips to prevent uneven effects in the two tubes.

Accuracy of the McLeod Gage

The accuracy of the McLeod gage when carefully calibrated is of the order of $\pm 0.5\%$. The capillary tubes are rarely more than 200 mm. long and the mercury columns are usually 100 to 150 mm. in length. The ability of the eye to set the mercury at a given zero mark and read heights is about ± 0.2 mm. Since there are two readings for each setting, this together with the uncertainty involved in the uniformity of the capillary bore, surface tension and wetting effects, causes the error to amount to 0.5 percent.

Extending The Range of the McLeod Gage

Several different designs have been used to extend the pressure range of McLeod gages. The gage shown in Fig. 127B is made up of two gages, both of which are filled from the same mercury reservoir. It may be calibrated by either of the two methods previously described. The gage is best

used for reading pressures in large systems where the compression caused by the mercury in the gage is insignificant. It should be pointed out that when the gage is used on systems of small volume the compression due to the mercury rise from the cut-off at the large bulb to the final mercury height must be considered. This gage can be made to have a range of 10^{-5} to 25 mm. of mercury.

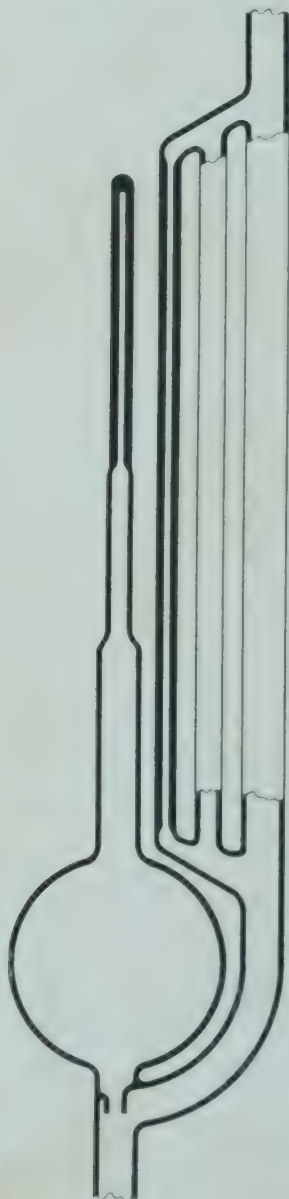


Fig. 128

Another gage design is illustrated in Fig. 128. The gas is compressed into a closed tube which is made up of three

different tube sizes.* The three side arms have diameters which are matched with each size of the closed tube. The gage must be calibrated and used as illustrated in Fig. 123C and the readings are made on a linear scale. The range of this gage is from 10^{-5} to 1 mm. of mercury.

In order to extend the sensitivity of the McLeod gage in the range of 10^{-4} to 10^{-6} , the use of Apeizon oil³ is recommended as a confining liquid.

A second method⁴ of increasing the sensitivity of the McLeod gage is by the use of a small Pirani or hot-wire gage in the closed end of the capillary. This gage is used after the gas is compressed in the capillary. The measured pressure of the gas as indicated by the Pirani gage is then converted to the original unknown pressure by using the known compression ratio of the McLeod gage. The combination of these two gages can be used to read pressures of various gases but a calibration of the gage for each gas must be obtained before measurements can be made. The limit of this gage when air was the confined gas, was, according to A. H. Pfund, 1.7×10^{-7} mm. of mercury.

It should be pointed out that the McLeod gage is based on the accuracy of Boyle's Law and when this is not valid, corrections for the deviations must be made. It cannot be used for measuring the pressure of condensible gases. Precautions also must be taken when certain gases are to be used as some will attack the mercury of the gage, particularly if there is a slight trace of moisture present. Gases which have a tendency to be absorbed on glass surfaces also give incorrect pressure readings.

The McLeod gage frequently is used for calibrating other types of vacuum gages. When used for such purposes, it is important that no gas be trapped at the mercury cut-off. A suitable slanted ring seal below the bulb is fabricated as illustrated in Fig. 129A and is assembled as follows:

1. An 8-mm. tube is opened on a diagonal in the gas burner flame. This tube is cut 8 mm. from the diagonal cut.

2. A 16 mm. tube is closed as shown in Fig. 129B. The angle of the closure should be approximately the same as that of the 8 mm. tube.

3. The small tube is ring-sealed into the larger tube and the bulb is sealed to the ring seal.

4. The 16 mm. tube is then opened at the extreme end and the side tube is sealed over the opening. The seals are

*EDITOR'S NOTE.—This multiple-chamber design with corresponding side arms is due to L. Dunoyer: *Bulletin Société Française de Physique*, 1923, page 246; also "La Technique du Vide" (book), 1924, pages 64-76. (English Translation "Vacuum Practice," London, 1926). For recent improvements in Dunoyer gage design see: P. Tarbès, *Le Vide*, Vol. 1, Jan. 1946, pages 9-11.—M. F. BEHAR.

then carefully annealed. When these seals are properly made, the mercury can be raised over the cut-off and the entire volume at the ring seal is completely filled.

BOURDON GAGES

Many other gages belong in the class which operate on the principle of balancing an unknown against a known pressure. These gages are used only when experimental studies are made with corrosive gases where mercury cannot be used, or when measurements must be made at temperatures considerably above room temperature. Gages of this type may be made sensitive to 0.1 or possibly 0.01



Fig. 129

mm. of mercury. The gage becomes quite fragile if it is made for high sensitivity.

A glass Bourdon gage is shown Fig. 130A. The thinwalled tube which is shaped in a semi-circle is deformed when a pressure gradient exists between the inside and outside of the tube. The gage is used as a null-point instrument since a known pressure must be used on one side of the tube to bring the unbalanced tube to a zero point.

The gage is made as follows:

1. The Bourdon tube is the most important part of the gage. A point is pulled on one end of a 10" section of 10 mm. tubing. A blow-tube is connected to the opposite end and the glass at the end of the tube is fused and closed. A 1" section of the tube, just below the closed end, is then fused sufficiently so that a thin-walled bulb can be blown. As the bulb is blown, it is stretched slightly to an oblong shape. It must be remembered that the sensitivity of the gage is dependent on the thickness of the bulb wall. However, if the bulb is

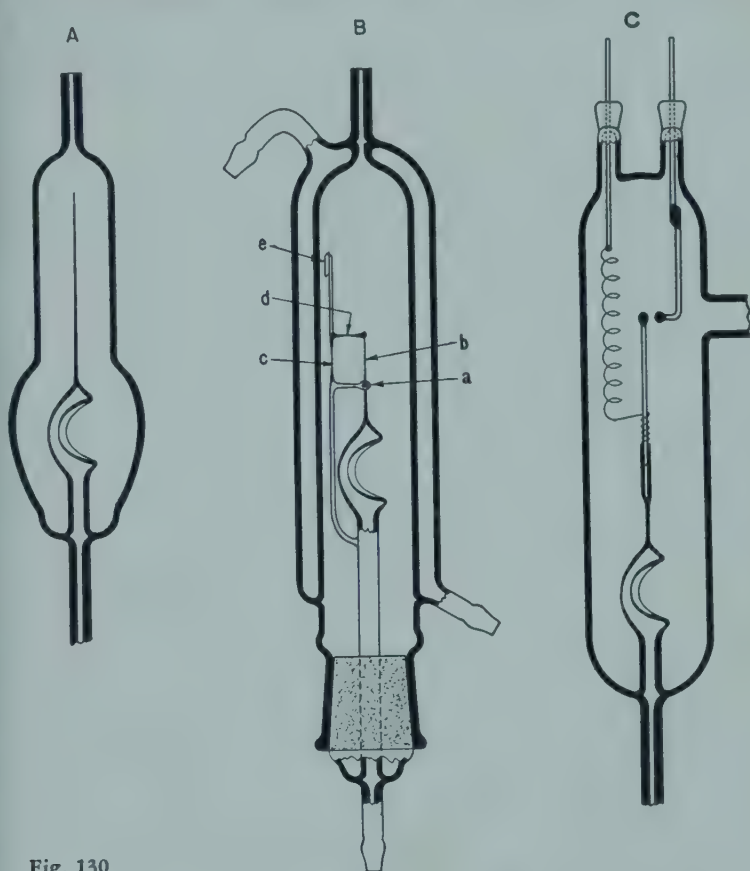


Fig. 130

too thin it will be too fragile. The bulb is then held perpendicular in a large brushy flame until one side of the bulb is collapsed. The radius of curvature of this side should be $\frac{1}{4}$ " to $\frac{1}{8}$ " less than the other side which is not fused. The sensitivity of the gage can be tested by blowing into the blow tube. The point at the tip of the curved tube should move about 3 to 4 mm. from the zero point. The original point is then cut from the tip of the prepared tube and a thin glass rod 6" long and 1 mm. in diameter is sealed to the tube. The 10-mm. glass tube is then cut 1" below the Bourdon tube and flared slightly for a ring seal.

2. The Bourdon tube is sealed into a 35-mm. tube after a fine glass point is drawn on the 1-mm. rod. A second glass rod with a fine point is sealed into the jacket. This thin point must be exactly in line and about 1 mm. from the thin point of the gage. An outlet tube is then sealed to the jacket. If the zero point and gage deflection is read with a low-power microscope fitted with an eyepiece scale, the second pointer is not necessary. The outside jacket should then be free of striations.

The gage must be used in a vertical position and the system is connected to the opening in the jacket. One leg of a mercury U-tube manometer is connected to the tube which is ring-sealed to the Bourdon tube. A pressure or vacuum on the outside of the gage will give a movement of the gage pointer. The pointer can be brought to the zero point by balancing this pressure with a pressure on the inside of the tube. This can be done by increasing or decreasing the pressure in the leg of the U-tube manometer by raising or lowering the confined manometer liquid. The pressure can then be read on the manometer.

A Bourdon gage designed by S. G. Foord⁵ is a modification of the single pointer gage. The movement of the glass tube is limited by a glass ring, *a*, Fig. 130B, which is attached to the glass tube with a glass rod. When pressure is applied, the movement of the pointer *b* deflects a thin fiber, 0.1 mm. in diameter, to which a small mirror is fastened. Tubes which are fabricated to withstand pressure changes of 1 atmosphere are used. The scale, one meter distant from the gage, can be used to measure the deflection of the gage, which is linear. A ground joint is used to aid in adjusting the lever system. The gage is also surrounded with a water jacket.

A Bourdon gage arrangement with platinum contacts mounted on the pointer and through the gage envelope is illustrated in Fig. 130C.

A second type of Bourdon gage was developed by S. G. Yorke⁶. The essential part of the gage is a thin-walled glass tube spiral. The mandrel arrangement for winding the spiral is shown in Fig. 131A. The gages shown in Figs. 131B and 131C are made as follows:

1. A 6-mm. tube 10" in length is heated in a ribbon flame and drawn to a diameter of about 1.25 mm. A 12" length of this tubing is then wound on a 5/16" diameter mandrel (carbon) which is slightly tapered. A small hole in the end of the mandrel is conveniently used for holding one end of the glass tube while the spiral is wound. This mandrel is mounted in a holder. A metal shield directly below the mandrel should be used to give even heat distribution. The flame is directed against this shield. The thin-walled tube collapses quite easily if it is heated directly

with a burner flame. The glass tube is inserted into the hole and the seven or eight turns are carefully wound on the carbon mandrel. The end of the spiral is then cut where it is connected to the mandrel and the spiral is removed.

2. The glass spiral is mounted in two ways. In Fig. 131B a pointer is sealed to the end of the spiral and bent at an angle of 90° to the spiral. The assembly is then ring-

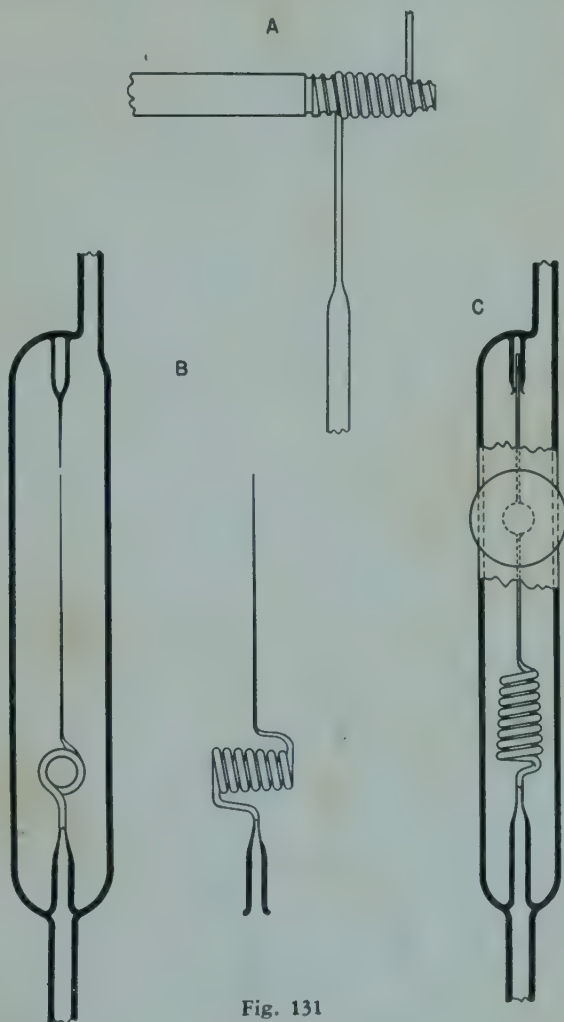


Fig. 131

sealed into a jacket. A small pointed glass rod is sealed to the opposite end of the jacket and adjusted in line with the spiral pointer. An outlet is then sealed to the jacket.

3. A second way of mounting the glass spiral, which is more accurate, is made as shown in Fig. 131C. The spiral is in a vertical position and the thin glass fiber pointer is supported at the top by a capillary tube. A small mirror

is fastened to the fiber with wax. An optical window is sealed to the jacket in line with the mirror. An increase of pressure inside the spiral gives a movement in the spiral which in turn moves the pointer from the zero point. The gage is balanced by increasing the pressure on the outside of the coil. The gage illustrated in Fig. 131C gives a deflection of 4 to 5 cm. at a distance of one meter from the gage for a pressure change of 10 mm. of mercury.

MOLECULAR GAGES

The vacuum or pressure gages which depend on the number of gas molecules or properties of these molecules are used quite extensively for industrial applications. Gages of this class are more recent in origin and nearly all of them require an electric circuit for measuring pressures.

Pirani Gage

The Pirani gage^{7, 8, 9, 10} is used quite extensively. It is simple to operate, small and can also be wired to electric controllers or recorders which in many cases is a definite advantage. This gage has the disadvantage that it is not an absolute gage as it must be calibrated with a McLeod gage for each particular gas.

The Pirani gage works on the principle of a change of resistance of a heated filament with a change in thermal conductance caused by the gas molecules in the gage. The filament is made of a material with a high temperature coefficient of conductance. Measurements are made on a bridge circuit. The pressure is determined by keeping the voltage constant and determining the magnitude of the current flowing through the filament or keeping the current constant and measuring the change in resistance of the filament. In practical operations a second gage under high vacuum is located in a comparative position of the bridge to act as a compensator. The bridge is held at constant voltage. The gage is evacuated to a high vacuum and the remaining two variable resistances are set so that zero deflection is obtained. The gage is then connected to the described system and, as pressure in the system increases, the bridge is unbalanced and current will flow through the galvanometer or microvoltmeter. The scale of such instruments can be calibrated in microns, giving the pressure reading directly. The Pirani gage is sensitive to 10^{-5} mm. of mercury but by special methods may be extended to 10^{-6} or lower.

The Pirani gage can be purchased from numerous manufacturers specializing in vacuum equipment. A gage compensated with a second gage under high vacuum can be obtained from Distillation Products, Inc., Rochester, New York. The Type PG-1A gage has a bridge unit and the vacuum is read on an indicating instrument which has two scales, 0 to 20 microns and 0 to 75 mm. of mercury.

Ordinary light bulbs of the show-case type, Fig. 132, can be used as a Pirani gage. Two bulbs are chosen which have nearly identical resistances. One bulb is used as a compensator in the bridge circuit. The other must be opened so that it can be sealed to the vacuum system. Since the bulbs usually are made of lime glass, a special technique must be employed for opening the bulb. A graded seal from lime glass to Pyrex glass (774) is made from 10-mm. tubing. The end of the bulb is opened by using a hot, pointed tungsten rod 0.04" in diameter. The end of the bulb is warmed slowly. The tungsten rod is then heated to a white heat and worked through the glass at the end of the bulb by spinning the hot rod with one's fingers. A small point is immediately pulled on the bulb and the glass is opened for the graded seal previously prepared, Fig. 132. The

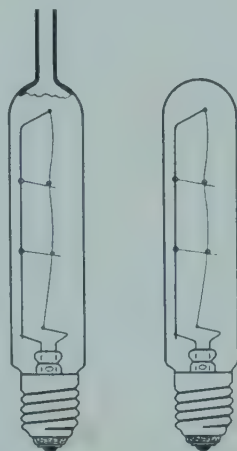


Fig. 132

bulb can then be sealed to the vacuum system through the graded seal. This bulb and the compensator bulb form the resistances for the two arms of the bridge while the other two resistances are of the variable type. A circuit for the gage is given in Fig. 133. The calibration curve of a typical gage is given in Fig. 134. The sensitivity of the galvanometer should be 10^{-8} amperes per scale division.

A small Pirani gage suitable for pressures up to 15 mm. of mercury was developed by E. S. Rittner¹¹. The body of the gage is made of 2 mm. Pyrex (774) capillary tubing. A 7-mm. tube of the same type of glass is sealed to the capillary for the outlet. The filament is 1-mil tungsten wire 3.5" long and is supported at each end by spot-welding to nickel foil which in turn is spot-welded to 0.04" tungsten rods. The 0.04" tungsten rods are covered with a sleeve of GT-70 glass and beaded with Nonex (772). A narrow band of uranium glass is sealed to the ends of the capillary. The tungsten rods are then sealed to the gage body.

This gage is used in a bridge circuit along with one 13-ohm and two 15-ohm resistors. A galvanometer with a sensitivity of 2.6 microamperes per scale division and 13 ohms internal resistance is used. A precision of $\pm 2.5\%$ is obtained in the pressure range of 10 microns to 15 mm. of mercury.

Thermocouple Gages

The thermocouple gage can be used in the pressure range of 0.1 to 10^{-4} mm. of mercury. The gage operates on a principle similar to that of the Pirani gage. The temperature of the hot filament is read by an auxiliary thermocouple which is welded to the filament. The gage requires a simple electric circuit with a constant-current source for the filament.

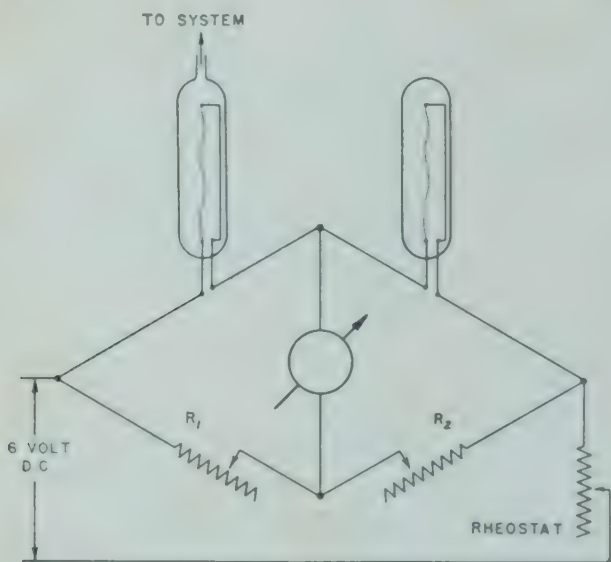


Fig. 133

The thermocouple gage designed by C. C. Dunlap and J. A. Trump¹² is shown in Fig. 135. The thermocouple is made of 3-mil Nichrome and 4-mil Advance wire. The entire length of this thermocouple is $2\frac{3}{4}$ ". The filament has the same length and is 4-mil platinum wire. The two thermocouple wires are first spot-welded together with low current and a short welding time. The couple is then spot-welded to the filament. The multiple press is made by first sealing a narrow band of uranium glass (3320) to Nonex (772). Pyrex glass (774) is then sealed to the uranium band and the former is cut and flared for the flare seal. The Nonex (772) section is then cut in the flame and a suitable press is made. Four press welds (nickel rod-tungsten rod-braided copper) are beaded at the tungsten

section by the procedure previously given for press seals. The bead glass is GT-70. The four beaded wires are then sealed in the prepared press. The nickel wires are then bent so that the four wires, two of the filament and two of the thermocouple, have an umbrella shape after they are spot-welded to the nickel support.

A standard 200 microammeter with an internal resistance of 60 ohms is used to measure the thermocouple current. A filament current of 150 milliamperes will give a thermocouple current of 150 milliamperes. The filament power source is 110 volts d. c. with a variable resistance to give currents from 100 to 200 milliamperes.

A typical calibration of this gage is given in Fig. 136. It will be noted that the sensitivity of the gage is best between the pressure range 0.1 to 0.008 mm. of mercury. It has been found necessary to degas the filament when it is exposed to atmospheric pressure by flashing the gage with four times the normal filament current.

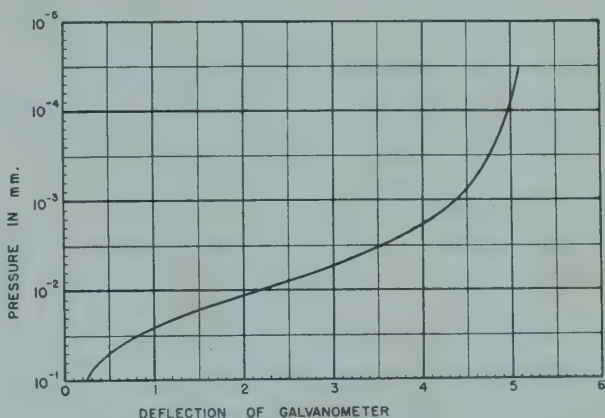


Fig. 134

A thermocouple gage is supplied by Universal X-Ray Products, Inc., Chicago, Illinois. This gage will indicate pressures down to 0.002 mm. of mercury and is useful for indicating or controlling pressures between backing and diffusion pumps.

The Knudsen Gage

The Knudsen absolute pressure gage¹³ operates on the principle of measuring the impact of molecules to which a certain amount of kinetic energy has been imparted by a heated filament. The gas molecules come in contact with the filament and, with the added energy gained by contacting the hot surface, impinge on a delicately suspended vane. The deflection of the vane gives a measure of the number of molecules—which is directly proportional to the

pressure in the gage. The Knudsen gage is sensitive to 10^{-8} mm. of mercury or better.

A gage of this type studied by J. E. Shrader¹⁴ and R. G. Sherwood was mounted in a Pyrex (774) tube 51 mm. in diameter and 9" long. The heating strip was platinum 0.018 mm. thick, 7.5 mm. wide and 18 cm. long. This heating unit is folded, forming a cross piece at the top, the two sides are spot-welded to 20-mil lead wires which pass through the glass in a glass-to-metal seal. The side strips are held in place by 15-mil tungsten wires mounted in a glass support. The movable rectangular vane is aluminum

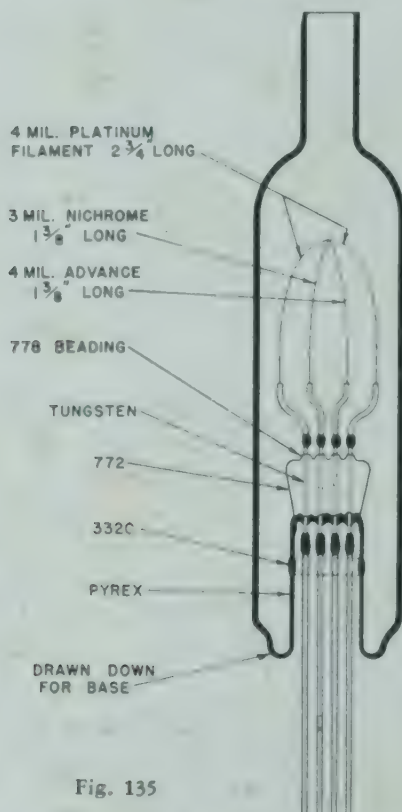


Fig. 135

0.0076 cm. thick and 0.5 cm. wide. The vane is mounted by passing aluminum wire through slots in the vane and suspended by 0.5 mil tungsten wire 6 cm. long. A mirror is mounted on the bottom of the vane. An electromagnet on the outside of the gage is used for damping the vane.

Knudsen showed that the pressure of the gage was given by the formula:

$$P = \frac{2K}{(T_1/T_2)^{1/2} - 1} \text{ dynes/cm}^2 \quad (13)$$

where K = a constant of the gage;

T_1 = absolute temperature of the heating strip;

T_2 = absolute temperature of the aluminum vane.

When small differences between T_1 and T_2 are employed, the equation for pressure becomes

$$P = \frac{4 K T_2}{T_1 - T_2} \text{ dynes/cm.}^2 \quad (14)$$

The temperature $T_1 - T_2$ is more conveniently expressed as

$$T_1 - T_2 = \frac{R_1 - R_2}{R_0 A} \quad (15)$$

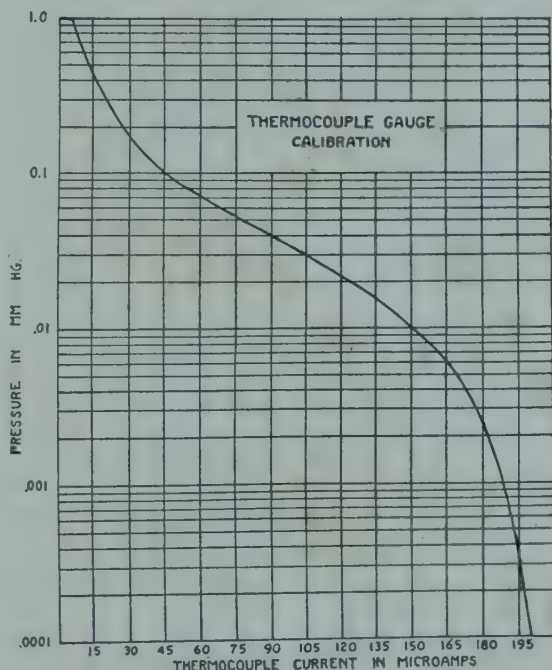


Fig. 136

where R_1 , R_2 and R_0 are the resistance of the heating strip at T_1 , T_2 and 0°C. , and A is the temperature coefficient of the heating strip. Substituting the value of $T_1 - T_2$ in equation 15 we have

$$P = \frac{4 K A R_0 T_2}{R_1 - R_2} \text{ dynes/cm.}^2 \quad (16)$$

The constant of the gage can be obtained from the physical dimensions of the gage or by calibrating it against a McLeod gage.

A Knudsen gage as described above indicates pressures down to 10^{-8} mm. of mercury when a temperature of 150° C. is maintained between the heater and the vane.

Several modifications of the Knudsen gage have been tested. J. W. M. Dumond¹⁵ and W. M. Pickels produced a gage which is satisfactory for routine measurements.

Ionization Gage

The ionization gage^{16, 17, 18, 19} is used for measuring vacua in the range of 10^{-3} to 10^{-8} mm. of mercury. This gage is essentially a triode and works on the principle of indicat-

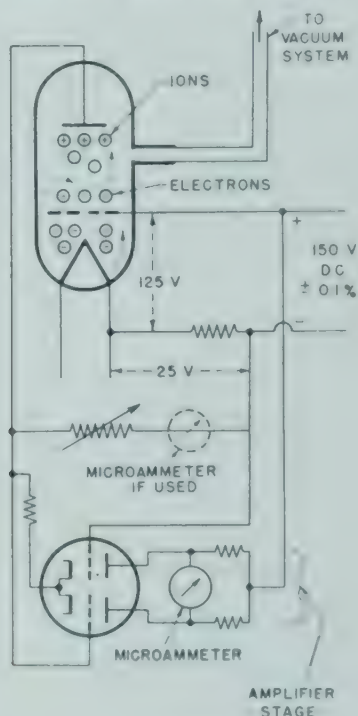


Fig. 137

ing the pressure as a function of the plate current. Electrons emitted from a hot filament in the tube are accelerated to an electrode, the grid, and the positive ions formed by the collision of these electrons and gas molecules are collected on a third electrode, the plate. The number of ions formed is directly proportional to the number of gas molecules in the tube and thus the plate current is a direct function of the pressure.

An electric circuit² which is used with the ionization gage is shown in Fig. 137. A voltage of 125 is applied between the filament and grid and 25 volts is applied between the grid and the plate. A constant filament current is maintained for electron emission.

A modification of the gage developed by R. S. Morse and R. H. Bowie²⁰ can be obtained from Distillation Products.

Inc., Rochester, New York. Data of this gage (VG-1A) are given in Table 19. The ionization gage is capable of recording the lowest vacuum attainable and electrical leakage and degassing problems are reduced to a minimum.

TABLE 19

PHYSICAL AND OPERATION DATA OF THE VG-1A IONIZATION GAGE

Collector	Thin film platinum
Grid	Spiral tungsten
Filament	Pure tungsten
Envelope	Pyrex Glass (774)
Height	3 $\frac{1}{2}$ "
Diameter	1 $\frac{1}{2}$ " O. D.
Tubulation	12 mm. O. D.
Filament	3.0-7.5 volts 3.5-5.0 amps.
Grid	+150 volts, 5 ma.
Collector	-25 volts, 120 ma./ μ

The ionization gage must be calibrated for each gas that is used in the vacuum system. A McLeod gage is used. Extreme precautions must be taken to prevent migration of mercury to the gage and that the pressures are equal through the entire system. A second disadvantage of the ionization gage is that the calibration curves are not linear above 10^{-3} mm. of mercury. The gage can be used only for short intervals above this pressure because of the danger of damaging the hot filament.

Several other ionization gages are commercially available. The National Union Radio Corporation, Newark, New Jersey, supply an ionization gage (Model Nu-R1038) which is capable of measuring vacua in the range 10^{-3} to 10^{-8} mm. of mercury and with a sensitivity of 1 microampere per 10^{-5} mm. of mercury. Another inexpensive gage (VG-2) is supplied by Distillation Products, Inc., Rochester, New York. Several ionization gage control circuits are also supplied by the latter distributor.

The Philips Ionization Gage

The Philips gage²¹ is used to read vacua by a principle of recording the ionization current produced by maintaining a high voltage across two electrodes in a tube. A powerful magnet causes the electrons to flow in spiral paths, thus increasing the probability and number of collisions with gas molecules. At low pressures a current of sufficient magnitude is obtained for measurements. Continuous indication is obtained and therefore the gage is quite useful in control systems.

The cathode or filament is preferably made of zirconium or thorium which give a copious supply of electrons when the filament is relatively cold. Since the filament is not hot while in operation, the gage is not damaged by the accidental admission of air.

The electric circuit consists of a transformer which will develop 2000 volts from a 110-volt 60-cycle power source, resistors and capacitors and a microammeter. The gage is calibrated for each gas with a McLeod gage.

The cold-cathode ionization gage, Model U-6000-1-2, supplied by the Universal X-Ray Products, Inc., Chicago, Illinois, will measure pressures in the range of 1.5×10^{-3} to 7×10^{-5} mm. of mercury. The Philips gage, Type PhG-1, supplied by Distillation Products, Inc., Rochester, N. Y., can be used in the pressure range 2.5×10^{-2} to 2×10^{-5} mm. of mercury.

All gages discussed under the second class are electrical in nature and are subject to the disadvantages encountered in electric circuits. On the other hand electrical gages can be remotely located and are easily incorporated in automatic or control systems. It is quite important that a study of each gage be made when one is required in routine or experimental work. Usually it is beneficial to increase the pressure range measurements by using several gages.

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CHAPTER XI.

HIGH VACUUM TECHNIQUE IN EQUIPMENT PRODUCTION

In scientific research, high vacuum has become a useful tool with which the scientist has solved various problems. In technology, electron-tube production, molecular or short-path distillation, surface area measurements of porous materials, rare-gas tube production and low-pressure studies of chemical reactions are just a few of the numerous applications in which high vacuum has played an important rôle.

The techniques required in using high vacuum are not difficult to master, especially if the fundamental principles are thoroughly understood. Misuse of vacuum systems can be costly; if certain precautions are not taken when systems are constructed, unreliable results will be obtained.

Two basic and fundamental requirements in the construction of a vacuum system are as follows:

1. Construction materials. The system should be made of materials which are capable of holding the desired vacuum.

2. Dimensional details. All connecting lines in the vacuum system should be large enough so that the pumping speed of the vacuum pumps are not reduced.

These two basic requirements are usually the cause of considerable trouble in vacuum systems and consequently a discussion of each is warranted.

CONSTRUCTION MATERIALS

Glass and metals have been the predominant construction materials for vacuum systems. Small laboratory systems are usually constructed from glass and it is toward such systems that the following discussion will be directed. Certain advantages are gained by using glass because anyone who has mastered the fundamental sealing operations can build suitable systems. The relatively low cost of glass, the ease at which glass systems can be changed, and visibility, are added advantages gained by using this construction material. When metals are used, machine shop facilities must be available and consequently the cost of construction will be higher. Metal systems have greater application in large commercial installations.

The plan of a glass vacuum system requires a certain amount of deliberate study. The evacuation problem should be reviewed and from its requirements a proper choice of condensation and forepump can be made. A discussion of matching speeds of these two pumps has already been given. The second consideration of the problem is the application of the vacuum system. If vacua approaching the ultimate

vacuum of the pumps are desired, it is good practice to eliminate all stopcocks, ground glass joints (either tapered or flat) and rubber hose connections on the high-vacuum side of the system, i.e., between the apparatus being evacuated and the vacuum pumps. Even though stopcocks and joints are ground to close tolerances, the lubricants for these ground surfaces have a vapor pressure which will in some cases be sufficient to prevent the attainment of high vacuum. The use of stopcocks, joints and rubber tubing between the condensation and fore pump is not as critical if the fore pump can maintain the required forepressure. Some vacuum systems are used to maintain a vacuum in a system which is not necessarily the ultimate vacuum of the pump combination. The evacuation problem then requires that the vacuum be maintained, not by preventing leakage or degassing in the high-vacuum side but, rather, by making the speed of the pumps great enough to pump the required vacuum. In this case it sometimes is impossible to eliminate all stopcocks or ground joints on the high vacuum side. It is good practice, however, to use the minimum number of stopcocks or joints.

The assembly of a glass vacuum system is not difficult if the parts are carefully planned and properly fabricated. All tube ends which are to be sealed should be smooth and square-cut so that when fused they can be perfectly joined. A minimum amount of working the glass is then required. If the ends are not smooth and perfectly joined, pin-holes are frequently obtained.

Leaks in a vacuum system caused by pin-holes are very disturbing and many times render the system useless. Various methods of finding leaks have been used. The simplest (though not the most satisfactory) has been the use of a Tesla coil. These coils are not expensive. It has been the authors' experience, however, that unless such coils are used with discretion, the damage that can be caused will lead to a great deal of work. Unless seals are made with uniform wall thickness, it is possible to punch pin-holes in the glass.

The best method for finding leaks is to use electrical gages as the Pirani¹ or ionization gage.² These gages are located between the condensation and fore pumps. The gage is balanced while the pumps are in operation and sections of the system are painted with acetone, carbon tetra-chloride or ethyl alcohol.³ Vapors are drawn into the system at the pin-holes and are registered by the gage. Directing a stream of a gas, such as hydrogen, over various parts of the system has been used to detect small pin-hole leaks.

Leak detectors employing the principle of the mass spectrometer⁴ have been successfully used in detecting leaks in vacuum systems. This instrument is attached to the vacuum system and, as the latter is pumped, a jet of helium is directed over various parts of the system. This gas is drawn

through the leak and passes through the mass spectrometer, where a definite recording is made of the gas with this mass. The operator can thus locate the section and the leak in a relatively short time.

DIMENSIONAL DETAILS

One of the most critical parts of a vacuum system is the cross-sectional area of the vacuum lines. Even though the proper choice of condensation pump is made and this pump is matched with a suitable forepump, the rated pumping speed (liters per second) cannot be obtained if the connecting lines are too small. If time is not an important factor and the problem is one of simple evacuation, ultimate pressures can be obtained through small tubes by long pumping periods. On the other hand, when the problem is one of maintaining a certain low pressure in a system where considerable gas must be pumped, one has no alternative but to use lines which are large enough so as not to decrease the pumping speed, especially when the desired speed of evacuation is close to the rating of the pumps. In order to determine or calculate the speeds that can be obtained through various tubes, it will be helpful to review briefly the theory of the flow of gas through a tube and to define pumping speeds of pumps.

Since a vacuum is obtained by actually removing gases from a closed system, it is important that the laws governing molecular motion be known in order that suitable systems can be built for obtaining low pressures.

The work of Robert Boyle and of Edmé Mariotte established the earliest quantitative behavior of gases. The law* derived from their studies states that at constant temperature the product of the pressure and the volume of a given mass of gas is equal to a constant. It can be shown by experimentation that Boyle's law is not exact and that the deviations from the law are slight at low pressures and disappear as the pressure approaches zero. Since low pressures are used in vacuum systems it is satisfactory to use this law.

Avogadro's hypothesis, which states that equal volumes of different gases, at the same temperature and pressure, contain the same number of molecules, has also been shown to be only approximate for actual gases. It is useful, however, to assume its validity when applied to systems at low pressures.

Boyle's law has been shown to be dependent on the temperature. The investigations of Charles and Gay-Lussac have shown the behavior of gas volumes at various temperatures. Data concerning the volume changes show that there

*Known as Boyle's Law in most English-language texts and as Mariotte's Law in all French and in some other texts.

are discrepancies among various gases, but that these discrepancies become slight at low pressures.

Combining the gas laws we may write:

$$PV = RT \dots \dots \dots (17)$$

where P = pressure on gas, dynes/cm.²

V = volume of gas, cm.³

R = "gas constant," for the particular gas

T = absolute temperature, °K.

This mathematical expression is known as the *equation of state* or the *characteristic equation* for a perfect gas. It predicts the behavior of an ideal gas and can be applied to actual gases only as the pressure approaches zero. At low pressures, encountered in vacuum studies, it will serve even better than is expected because deviations from the laws become small as the pressure approaches zero.

The kinetic theory states that the average velocity of the molecules of a gas increases as the temperature increases. As molecular velocities increase, molecular collisions are more frequent. If the molecular population is decreased, i.e., decreasing the pressure of a fixed volume of gas, each molecule travels a greater distance before it collides with another. The equation relating this distance, called mean free path, with the molecular population and molecular diameter is:

$$l = 1/(\sqrt{2} \times \pi n \sigma^2) \dots \dots \dots (18)$$

l = mean free path (cm.)

n = number of molecules per cubic centimeter

σ = molecular diameter (cm.)

It will be interesting to note how the mean free path increases with decreasing pressure. If the molecular diameter of nitrogen is taken as 3.13×10^{-8} cm., the mean free paths at various pressures given in Table 20 are obtained by calculation.

TABLE 20. MEAN FREE PATH OF NITROGEN

Pressure (mm. of mercury)		Mean Free Path (cm.)
760	8.51×10^{-6}
10	6.47×10^{-4}
1.0	6.47×10^{-3}
0.1	6.47×10^{-2}
0.01	0.647
0.001	6.47
0.0001	64.7

The mean free path increases rapidly with decreasing pressure and, in the usual vacuum range, it can be seen that collisions between molecules are relatively infrequent, whereas molecules collide more frequently with the walls of the confining vessel. The removal of gases from vessels through very small tubes can be expected to be quite difficult. If the resistance to flow of the gas at the end of the tube at the vacuum pump is designated by r , the resistance

at the end of the tube of l centimeter length as r_1 , and W as the resistance of the tube, the total resistance is given as:

$$r_1 = r + W. \dots \dots \dots (19)$$

The opposition to flow is inversely equal to the pumping speed:

$$r = 1/S_0, r_1 = 1/S$$

where S_0 = pumping speed at the pump
 S = pumping speed at the end of the tube 1 cm. from the pump.

Replacing these values of r and r_1 we have

$$1/S = (1/S_0) + W$$

or $S = S_0 / (1 + WS_0) \dots \dots \dots (20)$

M. Knudsen⁵ has shown that the resistance of gas flow through a tube is given by the following equation:

$$W = 1.59 \times 10^{-5} \left(\frac{273 M}{T} \right)^{3/2} \left(\frac{l'}{D^3} + \frac{4}{3D^2} \right) \text{sec./cm.}^3. \quad (21)$$

where M = molecular weight of the gas
 T = absolute temperature, °K.
 l' = length of connecting tube, cm.
 D = diameter of tube, cm.

This equation was found to be accurate to within 5% when the ratio of the diameter of the tube and the mean free path was as great as 0.4. The first term in the parenthesis is the resistance of the tube and the second term is the resistances of the two ends of the tube.

When air is pumped through a tube at room temperature equation 21 becomes:

$$W = l''/r^3 \text{ sec./liter} \dots \dots \dots (22)$$

where l'' = length of tube, mm.
 r = radius of tube, mm.

The resistances of the two ends of the tube were neglected in obtaining equation 22 and the tube resistance is expressed in sec./liter. This value for W can be used in equation 20.

The effective pumping speed of a condensation pump can be reduced by using connecting lines with small diameters on the high vacuum side. As an example, suppose that the speed of a condensation pump is 10 liters per second at 0.0001 mm. of mercury and that the connecting tube from the pump is 10 cm. long and has a diameter of 1.0 cm. The resistance of the tube is, according to equation 22

$$W = \frac{100}{125} = \frac{4}{5} \text{ sec./liter.}$$

From equation 20

$$S = \frac{10}{1 + 4/5 (10)} = 1.11 \text{ liters/sec.}$$

The effective pumping speed of the condensation pump is reduced to 1/9 of its rated speed.

The resistances of various different sized sections of a vacuum line are additive. If the line which is illustrated in Fig. 138 is used, a separate resistance for each of the three

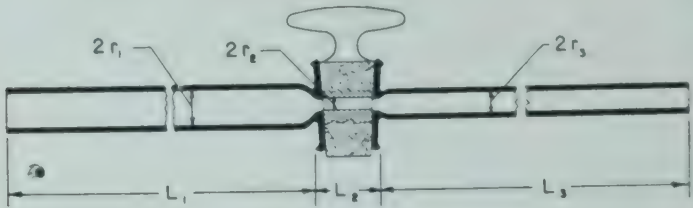


Fig. 138

sections must be calculated. The total resistance of the line is the sum of the three resistances. If $r_1 = 10$ mm., $l_1 = 20$ cm., $r_2 = 1$ mm., $l_2 = 0.5$ cm., $r_3 = 5$ mm., $l_3 = 10$ cm., the total resistance is

$$W = \frac{200}{1000} + \frac{5}{1} + \frac{100}{125} = 6.0 \text{ sec./liter}$$

If the speed of the pump is 10 liters per second the effective pumping speed at the end of the line containing the stop-cock is

$$S = \frac{10}{1 + 6(10)} = 0.164 \text{ liters/sec.}$$

This example definitely shows that the size of the connecting vacuum lines cannot be neglected if it is desirable to maintain the rated speed of the condensation pump. It is, therefore, good practice to use large and short lines between the condensation pump and the equipment being evacuated, even though it is not necessary to maintain the rated speed of the pump. It can also be shown that if low-speed pumps are used, the resistances of the vacuum lines are not nearly as important as in the case of high-speed pumps.

The speed of a pump is defined as the volume of liquid or gas that passes through the pump in unit time. This definition cannot be applied to a vacuum pump because under pumping conditions a continuous decrease in pressure is obtained in the enclosed system. The speed of the vacuum pump must therefore be defined as the relative rate of decrease of pressure in a fixed volume. If P_0 is the ultimate pressure limit of the pump and V the volume of the vessel being evacuated, the speed of the pump is defined mathematically as

$$S = -V \frac{dP}{(P - P_0) dt} \dots \dots \dots (23)$$

Integrating equation 23 we have

$$S = \frac{V}{t_2 - t_1} \ln \left(\frac{P_2 - P_0}{P_1 - P_0} \right) \dots \dots \dots (24)$$

where P_2 and P_1 are the pressures at t_2 and t_1 respectively.

Equation 24 can be used only for determining the speeds of pumps which have small limiting pressures. If P_0 is small in comparison to P_2 and P_1 it can be neglected and equation 24 becomes

$$S = \frac{V}{t_2 - t_1} \ln (P_2/P_1) \dots \dots \dots (25)$$

which gives the speed of a pump as defined by Gaede.⁶

The pumping speeds of condensation pumps can be determined experimentally by several procedures. The constant-pressure method is applied by using a constant-bleed valve. The volume of gas which passes through the valve is measured at atmospheric pressure. This volume, after pressure conversion, is plotted against time with pressure as the parameter. The method of determining pumping speeds developed by G. C. Eltenton⁷ is useful for quick tests of pumping speeds. H. C. Howard⁸ has also described a constant-pressure method which is recommended for high speed pumps.

Molecular Thermal Flow

M. Knudsen⁹ and G. West¹⁰ have shown that, at low pressures, molecular flow is obtained between two vessels if the temperature of one vessel is different from that of the other. The flow is from the cold to the hot chamber until equilibrium is established. The pressure ratio is given by the equation

$$(P_1/P_2) = (T_1/T_2)^{1/2} \dots \dots \dots (26)$$

where T_2 and T_1 are the absolute temperatures of the two vessels.

The application of equation 26 will be helpful when it is necessary to determine pressures in low-temperature reaction vessels which are maintained at low pressures. As an example: suppose that a vacuum system contains a chamber immersed in liquid nitrogen and that it is desirable to determine the pressure in this chamber. If the vacuum gage is connected to the cold chamber, thermal flow will be obtained to the gage envelope or bulb and the pressure indicated will be in error by $(77.3/298)^{1/2}$ or 0.5 of the gage reading.

CLASSIFICATION OF VACUUM SYSTEMS

Laboratory vacuum systems can be divided into two classes.¹¹ The first class, the static system, is used for obtaining the highest ultimate vacuum in various types of equipment. The entire system must be thoroughly out-gassed and be entirely free of leaks. The second class, the kinetic

system, is used primarily in systems where pressures of the range 10^{-3} to 10^{-6} mm. of mercury must be maintained. Systems of this class usually have high-speed forepumps and condensation pumps and consequently are used for equipment which, by its nature, cannot be leak-proof. Since each system is used for various problems in scientific research, a description of such systems and techniques involved will be given for each class.

Static Systems

Static vacuum systems are used in investigations which require vacua of the order of 10^{-6} to 10^{-9} mm. of mercury. Research in thermionic emission and photoelectric effects are but two of many examples which require a high vacuum. The glass blower finds that a good static system is indispensable in the production of vacuum-jacketed glass equipment.

One of the first and the most important items required in the assembly of a permanent glass vacuum system and



Fig. 139

yet the most neglected, is a proper method of clamping and mounting equipment. Rack clamps are frequently used. The authors have found that the clamps illustrated in Fig. 139 are most satisfactory and have a neat and compact appearance. These clamps are used with felt or asbestos pads which fit around the glass and serve to relieve strains when the clamp is tightened. The equipment clamps are made of brass or steel and the rod clamps are made of aluminum bar stock. Both are clamped in position with small flat-head screws which fit into the rod clamp. This clamp design allows one to have several clamps very close together on one rod of the rack.

A static system which has been extensively used for obtaining high vacuum is shown in Fig. 140. The clamps discussed above were used for mounting the assembly to the

box rack which is fastened rigidly to the wall. This rack is so arranged that all glass equipment is partly enclosed within the steel framework. All stopcocks are located below the McLeod gage within easy reach of the operator. The system is arranged as follows:

1. The high-vacuum manifold. The high-vacuum manifold extends from the extreme right across the top of the rack and down over the top of the table. Two mercury reservoirs and closed-end manometer filling tubes, previously illustrated in Fig. 122C, are connected to the high-vacuum manifold at the extreme right. A liquid-nitrogen storage Dewar flask, fitted with a silvered and vacuum-jacketed delivery tube, can also be seen at the extreme right. A strip-silvered Pyrex (774) Dewar flask is connected to the manifold. A clamp, fastened to the wall, is strong enough to support large and heavy equipment. A liquid-nitrogen trap is located between the equipment support clamp and the box-rack.

2. The McLeod gage. The McLeod gage is connected to the high-vacuum manifold just beyond the liquid-nitrogen trap. The gage in this system is the double McLeod gage previously illustrated in Fig. 127B. The glass reservoir to the right of the McLeod gage is connected to the mechanical oil pump through a stopcock. The reservoir can be evacuated by turning two stopcocks and thus vacuum for lowering the mercury in the McLeod gage is available during equipment evacuation without using the mechanical forepump.

3. Since it is necessary to have no stopcocks on the high-vacuum side of a static system, some means must be provided for isolating the high-vacuum manifold from the condensation pumps. To obtain a positive shut-off the mercury cut-off illustrated in Fig. 141 is used. A barometric leg between the mercury reservoir and the cut-off is used and mercury return lines prevent mercury from surging into the manifold or condensation pumps. Vacuum for lowering the mercury is obtained from the same vacuum reservoir which supplied vacuum for the McLeod gage. The mercury cut-off in Fig. 139 is located behind the McLeod gage panel.

4. Condensation pumps. The condensation pumps in the system, Fig. 140, have been illustrated in Fig. 105 and 107. The up-jet pump is located on the high-vacuum side and the down-jet pump is located on the low-vacuum side. The latter pump is connected to a glass surge reservoir and the mechanical oil pump.

5. Heating furnace. The furnace for heating glass equipment while it is being pumped is illustrated in Fig. 140. The furnace is built in sections which can be opened as illustrated. During the heating period the furnace is closed and



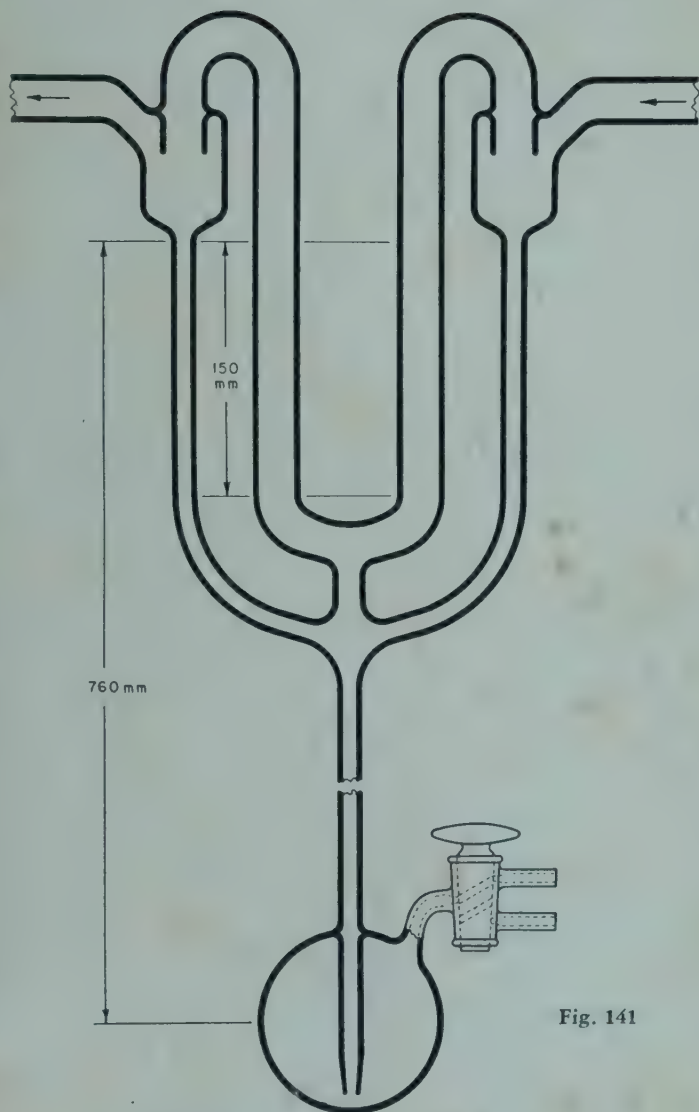


Fig. 141

a cover of Transite is placed over the top. When the equipment is tipped-off, the furnace can be opened as shown in the photograph. Equipment of various lengths can be pumped by using several furnace sections. The sections are set on a flat four-wheel cart. The temperature is controlled manually with the large Variac mounted on the wall to the left of the box rack.

6. Manometer and electric switch panel. Three indicating U-tube manometers are located on the panel. The one on the left is connected to the high-vacuum side of the system.

The middle manometer is connected to the vacuum reservoir used for lowering the mercury in the mercury cut-off and McLeod gage, while the manometer at the right is connected to the mechanical oil pump line. Three electric switches are used for the mechanical pump and the heaters of the two condensation pumps respectively.

7. Stopcocks. The stopcocks are all located on the mechanical pump side of the system. They are centrally located below the McLeod gage. Two three-way stopcocks are used for applying atmospheric pressure to the reservoir of the McLeod gage and the mercury cut-off. Two other stopcocks are used to close the forepump line to the condensation pumps and open this line to the auxiliary vacuum reservoir.

In concluding the description of this static vacuum system it should be pointed out that all manifolds are made of 25-mm. tubing. Liquid-nitrogen traps are located in the system to prevent migration of mercury vapor to the equipment being evacuated.

THE STATIC VACUUM SYSTEM IN EQUIPMENT PRODUCTION

Vacuum-jacketed vessels and columns are used extensively in scientific research. On many occasions when such special equipment cannot be purchased, the glass blower is asked to make parts or the entire assembly. For the sake of review and also to point out additional fabricating techniques and production, silvering, degassing and evacuation of vacuum-jacketed flasks and columns will be discussed.

Vacuum-jacketed flasks, commonly called Dewar flasks after their inventor, are useful for storing refrigerants such as liquid nitrogen or a dry-ice-trichloroethylene mixture. To minimize evaporation loss a double-jacket arrangement is used, Fig. 142C. The annular space between the inner and outer wall is evacuated after the walls are silvered. Such flasks can be made in various forms, the most common of which are the narrow-mouth and wide-mouth flasks. The steps involved for making these flasks are illustrated in Figs. 142A and 142B. The inner jacket is formed and the glass at the open end is spun into a flare which fits snugly into the outer jacket. The inner jacket is then centered in the outer jacket with two pads of fiber-glass ribbon. Streamers from these pads are required for their removal after the flare seal is completed. The assembly is then mounted as shown in Fig. 142B and the outer jacket is drawn down until the opening in the glass is about 10 mm. The excess glass is cut away in the burner flame and a 10-mm. tube is sealed to the opening. The tube is constricted in the burner flame until the opening is about 2 mm. and the wall thickness at the constriction is twice the original wall thickness.

When Dewars are to be strip-silvered, two tubulations are

required instead of the one, Fig. 148B. These tubulations are sealed to the bottom about one-half the distance from the center line of the Dewar and the outside wall. The center tube is then removed. The flask in the open furnace, Fig. 140, was constructed in this manner.

Distillation heads for low-temperature distillation columns are built on the principle of the Dewar flask. The cooling head of a low-temperature distillation column is shown in

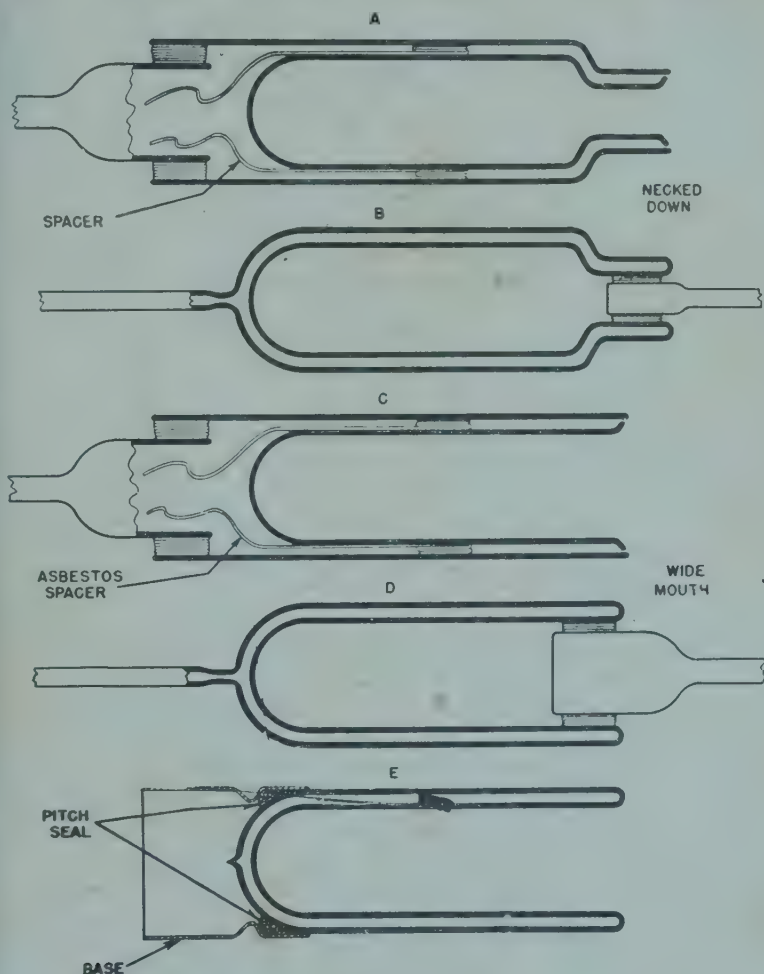


Fig. 142

Fig. 143B. The inner jacket is formed and a flare is spun on both ends. These flares should fit snugly into the outer jacket. The outer jacket, to which is sealed the tubulation, and the inner jacket are mounted on holders as illustrated in Fig. 143A. The holder for the inner jacket should be a tube of vitreous silica which will not soften when the large flare seal is made. A blow tube is connected to the holder

on the opposite end. The large flare seal is completed by fusing the glass, blowing it out and tooling it down with a carbon tool. The blow tube is then connected to the tubulation and the small flare seal is completed. Both seals are carefully annealed as soon as they are made.

A special condenser with a vacuum jacket is illustrated in Fig. 143C. The inner jacket is formed and a flare is spun on the open end. The outer jacket is made and a tube is sealed to the side. The spiral is sealed into the inner jacket and a short extension is immediately sealed to the ring seal. This extension is then flared. The outer jacket is slipped over the inner jacket and the entire assembly is mounted

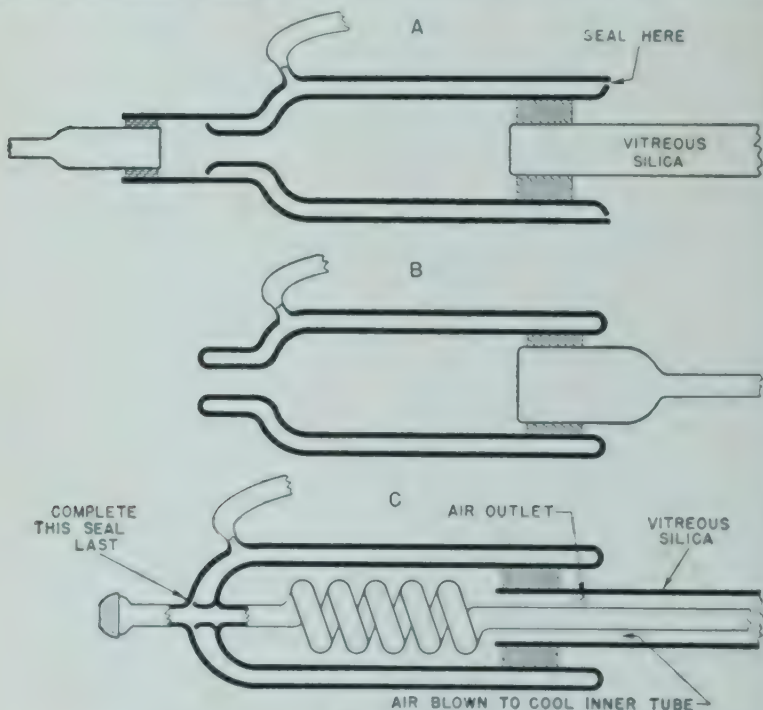


Fig. 143

on a vitreous silica tube which has a small hole behind the asbestos tape. As the flare seal is made, air is blown through the vitreous silica tube to keep the extension tube of the spiral from becoming too hot. The spherical joint is ring-sealed to the bottom of the jacket assembly. All seals should be annealed as soon as they are completed.

When large Dewars are needed with an outlet at the bottom, it has been found advantageous to insert a spiral between the inner and outer jackets. The contraction caused by the temperature differential when the refrigerant is poured into the flask is absorbed by the spiral. The flare seal is made first and the spiral is then ring-sealed to the outer jacket.

In all glass jacketed columns, two tubulations are required on opposite sides if the jackets are to be strip-silvered.

Vacuum-Jacketed Columns

Silvered vacuum-jacketed distillation columns must have some provision for the longitudinal expansion or contraction on the inner or outer tubes, because of the thermal efficiency of this type of insulation. There are various ways to prevent expansion breakage. The first is to match the expansion of the inner and outer tubes by using a vitreous silica tube which has a very low coefficient of expansion for the inner tube and Pyrex brand glass No. 744 for the outer jacket. This practice was recommended by Podbielniak.¹² A second method of matching expansions, especially in the temperature range 50 to 300°C., is to maintain temperature on the outer jacket so that the gradient across the two tubes is of the order of about 5°C. This is accomplished by using an electric heater on the outer jacket. Operation of the distillation column is thus complicated by temperature control. A third way of overcoming the disastrous effects of

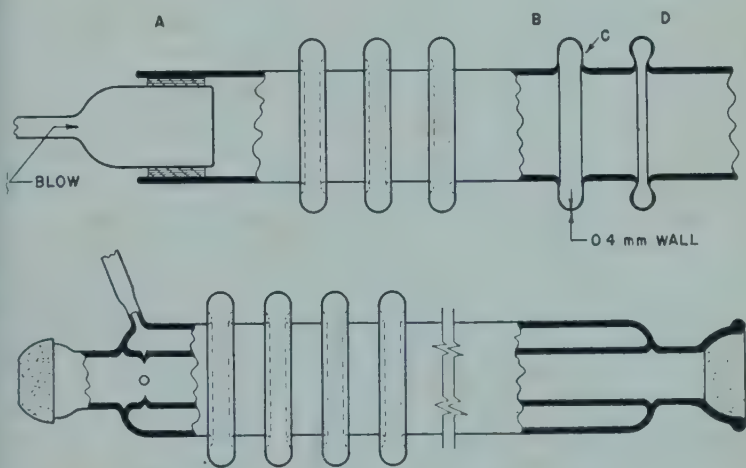


Fig. 144

unequal expansion is to provide a flexible glass section in either the inner or outer tube. Glass tube spirals have been used successfully on the inner tube. These spirals are sufficiently flexible to absorb the unequal expansion but offer the disadvantage of increasing the length of the column. Instead of spirals for the flexible tube section, it has been shown by D. J. Pompeo and E. Meyer¹³ that flexible glass bellows on the outside tube can be used with a great deal of success.

A glass-blowing lathe is required for the construction of glass bellows because the tube must be held perfectly centered. Since a short section of the glass is fused for each convolution, it is obvious that uniform wall thickness, which is essential in bellows construction, cannot be obtained in hand work. There are two forms of bellows. If the annular space between the inner and outer tubes of the column is about $\frac{1}{4}$ " the outside bellows must be used. This form of bellows has the disadvantage of extending out from the tube. The thin glass of the bellows is exposed and can be broken quite easily. However, guards can be made if necessary. The second form is the inside bellows.

Convolutions for the outside bellows are made as follows:

1. A section of tubing 51 mm. in diameter is chucked in the lathe. Several layers of asbestos tape should be wrapped around the tubing before it is chucked. This tape will prevent breakage if the tube is not entirely true, because the chuck tension is localized to about 1" length of the tube. A blow tube is connected to one end of the tube and the other is closed with a stopper.

2. A 2-cm. circular section of the tube is then heated while the tube is in rotation. The glass is then blown out slowly after the flame is removed and the tailstock of the lathe is moved so that the glass has the shape illustrated at B in Fig. 144. The glass is then allowed to cool for about four seconds and the blown section is pushed together until the shape illustrated at D in Fig. 144 is obtained. It is possible to form the glass in this manner because the glass at point C, Fig. 144, retains heat longer since it is thicker and closer to the tube than the glass at the periphery of the bellows. Properly-made bellows require precision timed movement in their formation with due regard to control of the viscous glass.

It has been found that the wall thickness of the bellows at the periphery should be about 0.4 mm. for best results.

3. Additional bellows are made by moving the burner 20 mm. from the first and repeating the above operation.

4. The entire assembly should then be carefully annealed.

Convolutions for an inside bellows are made as follows:

1. The glass tube, 51 mm. in diameter, is chucked in the lathe as described above. The blow tube is not required.

2. A 10-mm. circular section of the tube is evenly heated and stretched to 20 mm. as shown at A in Fig. 145. This thin section is then tooled down with a 6 mm. carbon rod to a depth of 10 mm. as shown at B, Fig. 145. The shoulder at B is then heated with a Hoke hand torch and the tailstock is moved 5 mm. toward the head chuck. The shoulder on the other side of the convolution is then heated and the tailstock is moved 5 mm., completing the convolution as shown at D, Fig. 145.

3. Additional convolutions of the bellows are made as above with 20 mm. between each. The entire bellows is then carefully annealed.

It has been found that five convolutions are sufficient for columns 18" long when inner tube temperatures up to 350°C . were obtained. For columns 48" long, seven convolutions, Fig. 145E, have been successfully used on columns where inside tube temperatures of 300°C . were used. In both cases the difference in temperature between the inner and outer tubes was about 200°C .

The production of bellows requires a technique which can only be gained through experience. The most important thing to remember is that the wall thickness of original tube and of formed convolutions should be uniform. The wall thickness of the convolution at C, Fig. 145 should be 0.4 mm. with a gradual increase to 0.8 for the glass at the shoulder C. The size of the convolutions for the bellows need not vary

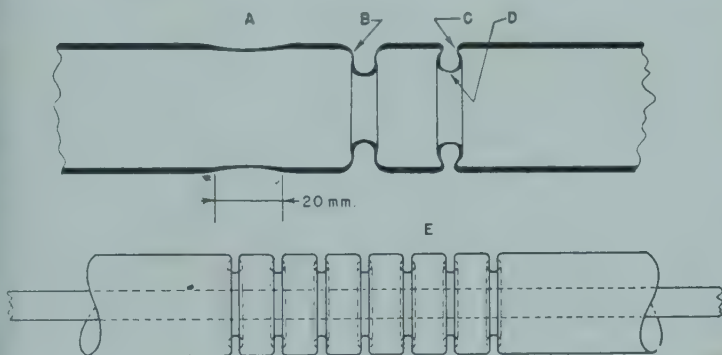


Fig. 145

much with different tubing sizes except when certain convolution depths are required.

Long column sections are sometimes required in distillation problems. The production of jackets, of the order of 120", is possible but equipment of this size becomes quite cumbersome. Jackets with overlapping sections, Fig. 146,

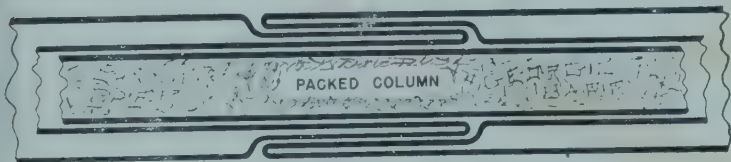


Fig. 146

are convenient. A thin layer of asbestos tape in the lapped section prevents glass-to-glass contact and yet allows for a certain amount of flexibility. Each section of the jacket can be made with bellows so that the expansion is compensated

in that section.

Silvering Vacuum Flasks and Jackets

Silver-plating the walls of vacuum-jacketed glass equipment increases their heat-insulating properties greatly—in some cases enormously. R. B. Scott, J. W. Cook and F. G. Brickwedde¹⁴ studied techniques for silvering Pyrex brand glass No. 774 and found that equipment made of this glass

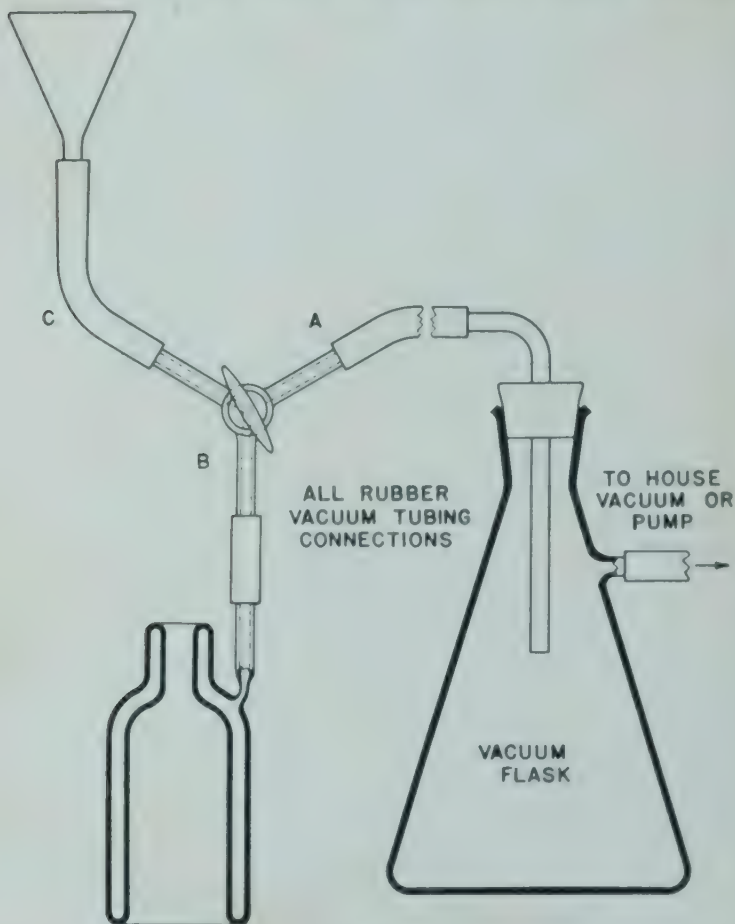


Fig. 147

could be successfully plated by adjusting the proportions and reagents of the Brashear formula. Their formula has been used successfully in this laboratory and for convenience will be outlined from their work.

Means of Introducing and Removing Cleaning and Silvering Solutions. In all equipment which is to be silvered, some provision must be made for introducing silvering solutions. Since such equipment generally is also evacuated, the opening for introducing the silvering solution can also serve as

a tubulation through which the jacket is evacuated. It has been pointed out before that the tubulation must have a constriction near the vessel in order that it can be properly tipped off. This constriction will cause some difficulty when introducing cleaning and silvering solutions unless some special expedient is used. The system illustrated in Fig. 147 is very convenient for adding and removing liquid from a jacketed vessel. The three-way stopcock is clamped to a rigid stand. Vacuum on the suction flask is supplied by a pump or house vacuum. The jacket can be evacuated by turning the stopcock connecting lines A and B, Fig. 147. The solution can then be added by filling the funnel and turning the stopcock until lines C and B are connected. Solutions can be removed by turning the stopcock connecting lines B and A.

The Silvering Solutions. The three solutions required for silvering glass equipment are prepared as follows:

1. Fifty grams of silver nitrate (AgNO_3) are dissolved in two liters of distilled water. This solution should be stored in a clean bottle and kept in a dark place.

2. Ninety grams of potassium hydroxide (KOH) are dissolved in two liters of distilled water. This solution is also stored in a clean bottle. No storing precautions are necessary except that the bottle should be kept stoppered when not in use. The solution improves with age.

3. Eighty grams of cane sugar are dissolved in 800 ml. of distilled water. A solution of 3.5 ml. of nitric acid (HNO_3) with a specific gravity of 1.42, in 100 ml. of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is added to the sugar solution.

The silvering solution consists of 16 volumes solution 1, 8 volumes solution 2 and 1 volume solution 3.

Cleaning Equipment Prior to Silvering. Glass equipment which is to be silvered should be carefully cleaned. The jacket tubulation is connected to the system shown in Fig. 147, and evacuated with house vacuum. Cleaning solution (sodium bichromate dissolved in sulphuric acid) is then allowed to flow slowly into the jacket. The temperature of the cleaning solution should be about 80°C . All surfaces should be covered with the cleaning solution for a period of 30 to 45 minutes. This solution is then removed and the jacket is washed six times with distilled water. The jacket is then filled with distilled water.

Silvering Flasks or Jackets. The water in the jacket is not removed until the silvering solution is prepared. In fact, it is advisable to keep all surfaces wet to obtain a good silvered surface. The silvering solution is prepared by using a sufficient amount of solution 1. Concentrated ammonium hydroxide is added to this solution from a burette while the solution is stirred. The ammonium hydroxide is added until

the precipitate which first forms just disappears. The required amount of solution 2 is then added. A dark brown or black precipitate is formed. (If insufficient ammonium hydroxide is added to solution 1, a yellow-green precipitate formed at this stage indicates that the solution has not been properly prepared. When this occurs the entire solution should be discarded.) Concentrated ammonium hydroxide is then added to the solution 1 and 2 until the brown-black precipitate is almost, but not completely dissolved. The solution can be used immediately or up to an hour after the solutions are prepared.

The water is removed from the jacket and the mixture of solutions 1 and 2 is allowed to flow into the jacket. The required amount of solution 3 is added in like manner and the contents of the jacket are shaken to insure complete mixing of solution 3 with the remainder of the jacket contents. Silvering time usually is from 10 to 30 minutes. The jacket should be rotated gently to insure silvering of all surfaces. The silvering solution is tested from time to time to ascertain whether silvering is completed. These tests are made by removing a small amount of the solution and noting the nature of the precipitate. A flocculent precipitate indicates that the silvering is completed. The solution is then removed and all sediment is carefully washed out of the jacket. The water is then removed by pumping with a cold trap between the pump and jacket. Brickwedde¹⁴ and co-workers found that by repeating the silvering operation a better silver plate could be obtained, especially if the first silver plate was not completely opaque.

Strip Silvering.

On occasions it is desirable not to plate a certain portion of the jacket surface. Usually, to gain the maximum reflectivity and yet have some of the surface free of silver plate it is more convenient to silver both sides and leave a narrow unsilvered section along each side of the flask. Columns and flasks of this nature can be used for high temperature ($200^{\circ}\text{C}.$), but are more efficient at low temperatures when the center of the tube is subjected to temperatures of to $-40^{\circ}\text{C}.$

Strip silvering is carried out in much the same manner as the operation discussed above except that two tubulations are required, Fig. 148B, and the silvering solutions 1, 2 and 3 are mixed before the solution is allowed to flow into the flask. The jacket walls must also be completely dry before the solutions are transferred to the jacket. The jacket must have two tubulations and it must be supported rigidly. The solution is then forced to flow slowly with gravity into the jacket through A, until the desired level is reached, Fig. 148. The solution is removed after the silvering is complete.

and the jacket is dried carefully before inverting. After the silvering is complete on the other side, the jacket is carefully washed and dried by evacuation.)

Evacuating Glass-jacketed Equipment

(The vacuum that can be obtained and maintained in glass vacuum jackets depends on the method adopted for the evacuation and heating of the equipment. Glass has a tendency to retain various gases and water, which are released at appreciable rates only under heat treatment. If a glass jacket is heated to a temperature near the softening point while it is being pumped and then sealed, a good vacuum will be maintained only for a short time. Gases which have diffused to the surface are retained in part at the surface and are released slowly. The vacuum in the jacket is thus

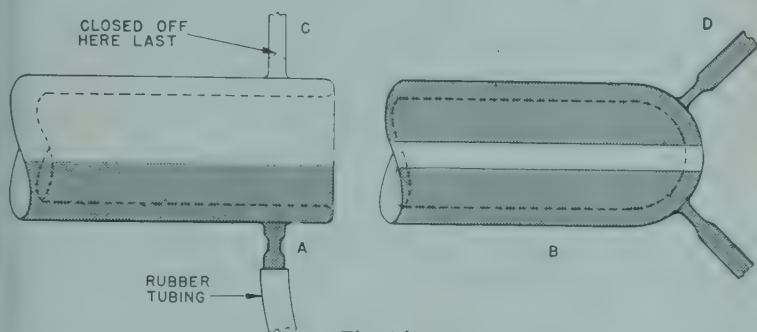


Fig. 148

gradually lost and the heat-insulating properties become poor. If the temperature is decreased 100°C . or so from the maximum temperature and pumping is continued, these gases on the glass surface can be pumped out, in part, and better vacuum jackets are obtained. There are, therefore, two phases in the heating and pumping process. The first consists in removing absorbed gases as well as forcing gases to the surface of the glass. The gases at the surface are then pumped from the jacket while the glass is hot.

Irving Langmuir¹⁵ has carried out extensive investigations concerning the heating and evacuation of glass bulbs used for incandescent lamps. Results of this work showed that lamps evacuated at 550°C . and then at 400°C . gave a lamp life of 900 hours as compared to 575 and 300 hours for lamps heated to 450 and 550°C . respectively. The conclusions drawn by Langmuir were that evacuation should be carried out in two or more stages of decreasing temperature.

Investigations of gases evolved from glasses were made by R. G. Sherwood¹⁶ and J. E. Shrader¹⁷. The results of Sherwood's work with soda, lead and Corning glass G-702-P are graphically shown in Fig. 149. The curves for each glass

give the total gas liberated from a glass surface of 350 cm.². Gas evolution reaches a first maximum at 150, 200 and 310° C. for soda, lead and Corning glass G-702-P respectively. The gas evolution then decreases and again rises at a temperature above the softening point of the glass. Sherwood concludes that the first maximum is obtained by the release of absorbed gases while the actual decomposition of the glass, liberating mainly water vapor, is responsible for the evolution at the higher temperature.

The history of the glass treatment also has some bearing on gas evolution. R. G. Sherwood and I. Langmuir both have found that (annealing glass at high temperatures greatly reduces subsequent gas evolution.)

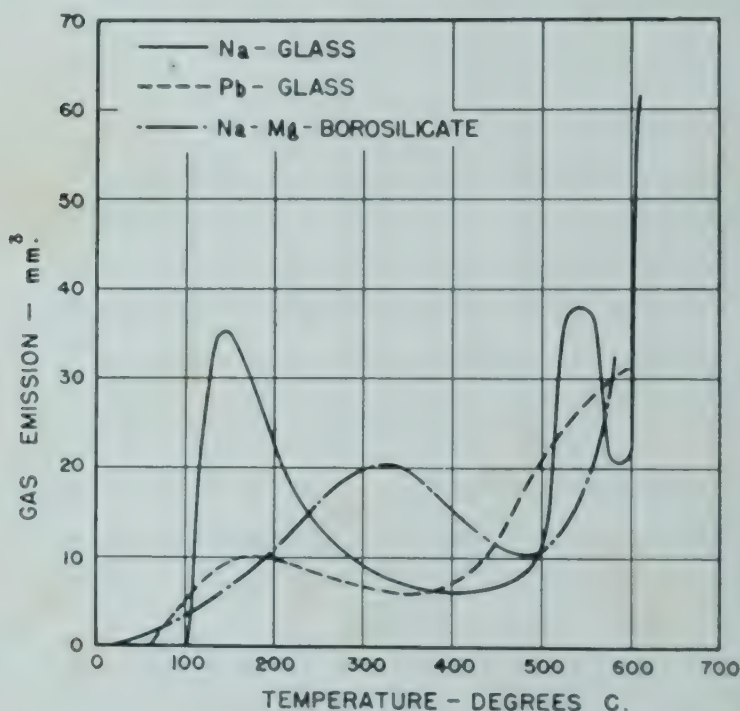


Fig. 149

The vacuum system shown in Fig. 140 is ideal for evacuating glass-jacketed equipment. The furnace sections can be so arranged that long as well as short equipment can be entirely enclosed by using several or just one hinged heater section.

The glass is baked and evacuated as follows:

1. It is advisable to clean unsilvered jackets with cleaning solution and to rinse several times with distilled water before evacuation. The jacket is then dried at room temperature by repeatedly evacuating and filling with dry air. A mechanical pump can be used if a cold trap or drying tube

is used between the jacket and pump.

2. The tubulation of the jacket is then sealed to the vacuum system manifold. The jacket is supported in the furnace in such a way that the glass blower can reach the tubulation without removing the entire furnace. If the jacketed equipment is not too heavy it can be suspended in the furnace and held in place by the tubulation. Heavier equipment is supported in such manner that the movement of the equipment is possible when the tubulation is closed by heating and drawing it to a tip. A method of supporting a strip-silvered Dewar is illustrated in Fig. 140.

3. The forepump is started and allowed to pump alone until the minimum vacuum of the pump has been reached. The trap is then cooled with liquid nitrogen and the condensation pumps are started.

4. When a vacuum of 10^{-7} mm. of mercury is obtained, the furnace heater is turned on. The temperature can be increased rapidly when unsilvered equipment is evacuated. A temperature rise about 1.2°C. per minute is required for silvered jackets. The temperature is raised to 550°C. when Pyrex brand glass No. 774 is being heated and maintained at this temperature for one hour. The temperature is then allowed to drop to 400°C. The equipment is pumped for 30 minutes at this temperature. The McLeod gage reading now should be better than 10^{-5} mm. of mercury.

5. The tubulation is sealed in two operations. The constriction is heated around the entire circumference and it is allowed to close slightly. The heating is stopped and four minutes are allowed for the removal of gases liberated from the hot constricted walls. The glass at the constriction is then heated and collapsed as the jacket is drawn away from the manifold. The tip is then rounded and annealed. The jacket is removed from the furnace and cooled as quickly as possible. Some discretion must be used in cooling hot equipment: if uneven contraction can be set up in critical regions as the condenser illustrated in Fig. 143C, the strains set up between the rapidly-cooling glass and glass that is not cooled are great enough to cause breakage. On the other hand, it has been shown by experiment that gases are liberated at high temperatures. It is important, therefore, to decrease the time so as to reduce the gas evolution to a minimum. Even under ideal conditions, gas evolution can be expected to a minor degree at room temperature.

Rare-gas Discharge Tubes

Rare-gas discharge tubes have become exceedingly important and on many occasions the glass blower is called upon to make them. In general the greatest application of such tubes is for lighting and display purposes. However, discharge tubes are also used as sources of light with defi-

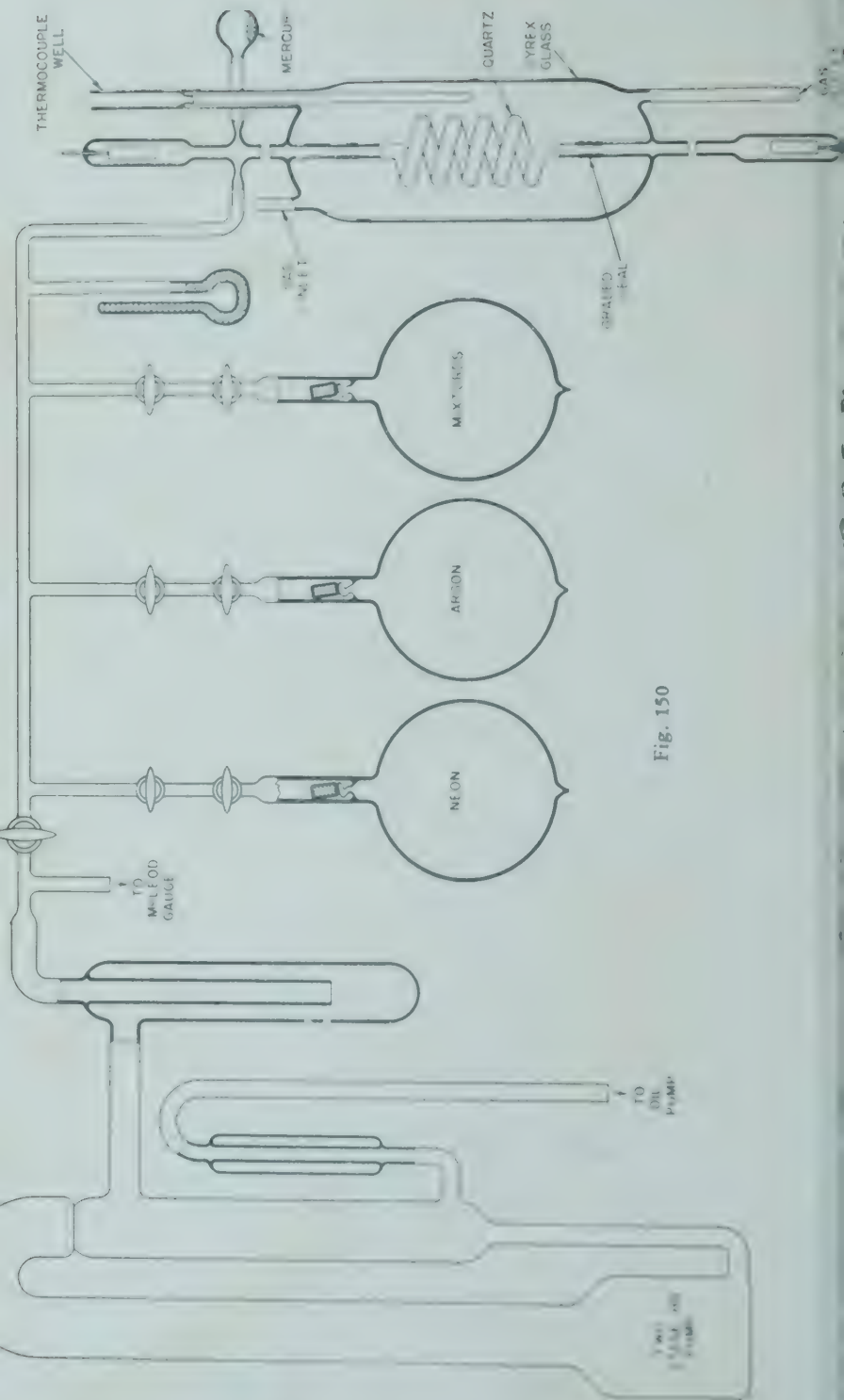


Fig. 150

nite wave-lengths. It has been found that the mercury ultra-violet lamp is useful for promoting various photochemical reactions. Many different lamps may be designed for such studies. The lamp and reaction chamber combination designed by E. Staecie and N. Phillips¹⁸ is simple and compact and is useful where a source of light is required with a wave-length of 2,537 Angstroms. The construction of this lamp will be given as an example of rare-gas lamp production.

A major requirement for discharge tube production is a good vacuum system. It is necessary to have a suitable source for filling the tubes with rare gas and convenient to combine the vacuum and rare-gas filling system into a single unit such as illustrated in Fig. 150. Special attention is called to the rare-gas storage flask. These flasks filled

with rare gases or mixtures are supplied by the Linde Air Products Company. The gas-filled flasks are obtained with a special capsule closure which can be opened by dropping a small pellet on the capsule. Since it is important not to contaminate the gas with any impurities it is necessary to use a pellet which can be thoroughly cleaned. Such a pellet can be made by sealing an iron rod, $\frac{5}{16}$ " by $\frac{3}{4}$ ", into a glass tube. This pellet will be heavy enough to break the capsule when it is dropped from a height of 3" and it can be cleaned quite easily.

The gas-filled flask can be sealed to the system as illustrated in Fig. 150. The two stopcocks are useful for controlling the flow of gas into the evacuated tube. If large amounts of gases are used it is sometimes convenient to use the arrangement illustrated in Fig. 151. The gas flasks can easily be changed because of the interchangeable ground joint and different glasses can be used, *i.e.*, soda glass on the flask and Pyrex (774) on the system.

In the production of the ultraviolet lamps, it is necessary that the glass of the tube transmits light in the range of the required wave-length. Transmission curves of vari-

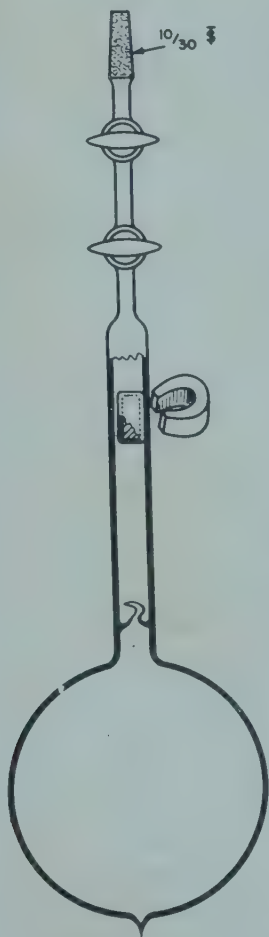
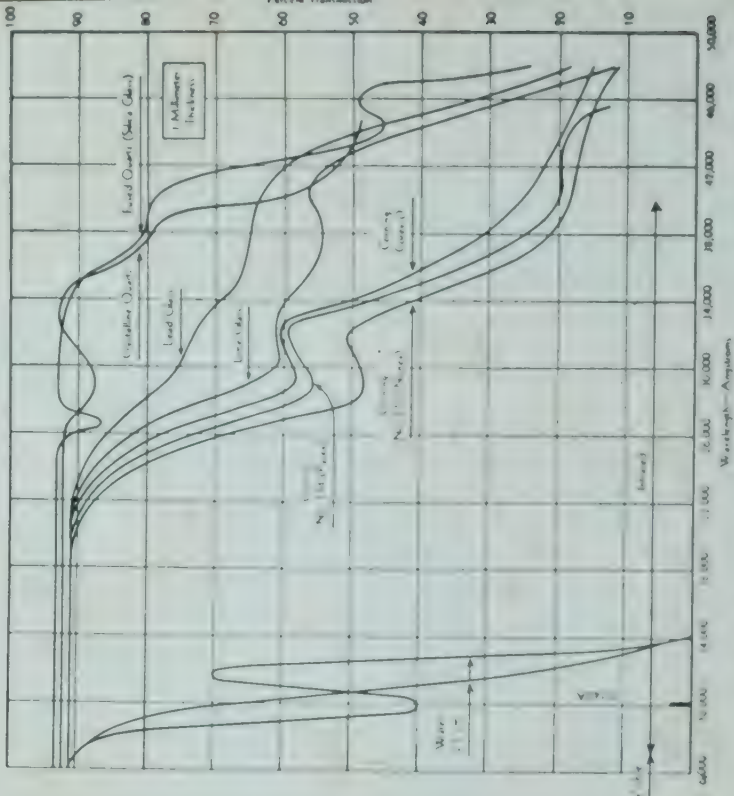
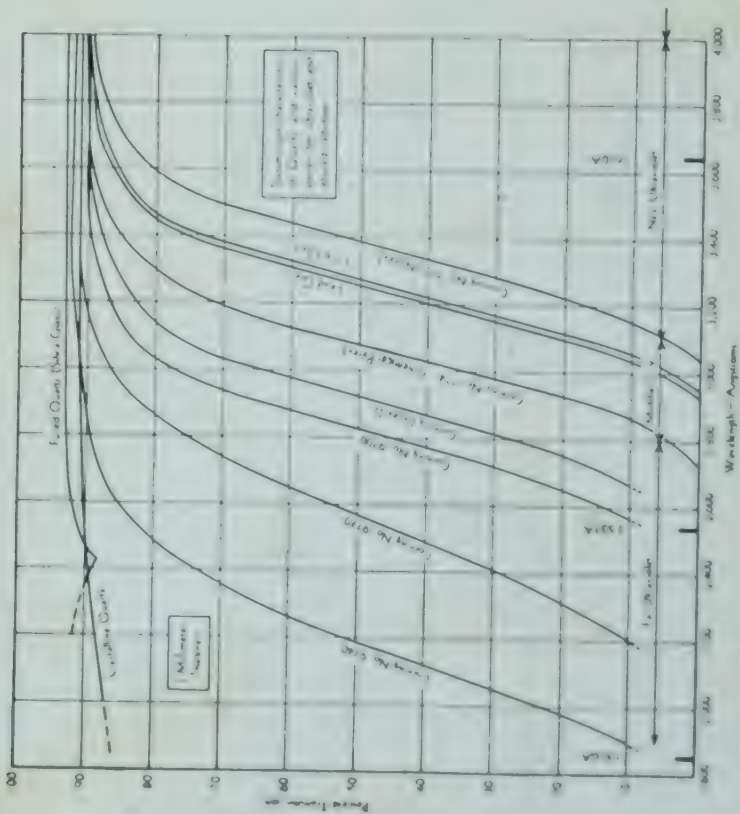


Fig. 151



ous glasses are given in Fig. 152. The material which is best suited for transmission at the wave-length, 2537 Angstroms, is vitreous silica.

Production of the Mercury Ultraviolet Lamp

The mercury ultraviolet lamp is made as follows:

1. A coil is made of 10-mm. clear vitreous silica tubing. The Hoke torch with a large jet is used with oxygen and acetylene as fuel to furnish the heat required to shape vitreous silica. A coil of 10 complete turns is made by the method previously outlined.

2. Since it is necessary to make the coil only of vitreous silica and the remainder of the reaction vessel of Pyrex glass No. 774, graded seals must be used at both ends of the coil. It is quite difficult to make a graded seal from vitreous silica to Pyrex glass No. 774 because of the high temperatures that must be used and because the seals between the successive glasses must be thin. The glasses used are vitreous silica and Corning glasses No. 790, 723, 720, 724 and Pyrex glass No. 774 in the order given. Graded seals which can be used for sealing vitreous silica to Pyrex glass No. 774 can be purchased from Corning Glass Works.

The graded seal is sealed to both ends of the coil and the Pyrex glass No. 774 is shaped for the lamp. The procedure for completing the lamp is now similar to that previously outlined for making a condenser. The thermowell is sealed into the jacket after the first ring seal and side tube seal is completed. The second ring seal is completed and the side arm is sealed to the jacket.

3. The preparation of the electrodes in the production of the glass-to-metal press seal will not be given here because it has been discussed previously. The electrode assemblies are sealed to both ends. Standard coated neon sign electrodes can be used; they are quite inexpensive. A tubulation for evacuating the lamp and a small reservoir containing a droplet of clean mercury are sealed to one end of the lamp directly opposite each other and below the electrode seal.

4. The lamp is now ready for evacuation, degassing and filling. It is sealed to a manifold in the position shown in Fig. 150. The lamp is evacuated to the lowest possible pressure along with the manifold and space above the closed capsule of the neon storage tube. The stopcocks above the neon storage tubes are then closed and the capsule is broken by raising the glass-covered iron pellet with a magnet and allowing it to fall. The tube is then filled with neon to a pressure of 20 mm.

The electrodes and the glass tubes of the lamp are now ready for bombardment. The leads of a 3.5-kva. 12,000-volt transformer are connected to the two electrodes. A heavy

TABLE 21. RARE GAS COLOR CHART

Color of Tube	Rare Gas	Glass Tubing	Mercury	Filling Pressure, mm. of mercury	Electrodes recommended
Deep Red	Neon	No. 240	No	6-12	Copper, nickel, iron or SVEA metal
Red	Neon	clear glass	No	6-12	Copper, nickel, iron or SVEA metal
Orange	Neon	No. 353 (Noviol)	No	3-6	Special chemically- treated
Golden yellow	Helium	No. 335	No	3-6	Special chemically- treated
Light green	*argon-neon mixture Linde No. 20 or 70	No. 333	Yes	6-12	Nickel, iron or SVEA metal
Dark Green	*argon-neon mixture Linde No. 20 or 70	No. 353 (Noviol)	Yes	6-12	Nickel, iron or SVEA metal
Light blue	*argon-neon mixture Linde No. 20 or 50	clear	Yes	6-12	Nickel, iron or SVEA metal
Dark blue	*argon-neon mixture Linde No. 70	No. 552	Yes	6-12	Nickel, iron or SVEA metal
White	Helium	clear	No	34	Special chemically- treated

* Argon-neon-helium mixtures must be used when the tubes are subjected to extreme winter conditions.

piece of bond paper is held against the tube. The tube is bombarded until the paper begins to scorch. In the bombardment, the electrodes are degassed and impact of gas molecules with glass walls tends to remove absorbed gases as well as moisture from the glass itself. The tube is then evacuated to a pressure below 10^{-5} mm. of mercury; isolated from the vacuum pumps by closing the main stopcock; and finally filled with neon to a pressure of .12 mm. of mercury. The tubulation is then uniformly heated at the constriction until the glass begins to soften. The tube is drawn away from the manifold as the glass collapses at the constriction. The glass is cut in the burner beyond the center of the closed section and the tip-off is carefully annealed. A drop of mercury is then transferred to the tube and this second tubulation is closed. The finished lamp is shown in Fig. 153. The appearance of the tube in operation with the electrical source mentioned above is shown in Fig. 154.

The intensity of radiation of this mercury ultraviolet lamp can be determined by the photohydrolysis of chloroacetic acid. E. Rudberg¹⁹ and Smith, Leighton and Leighton²⁰ have outlined experiments to determine the photochemical effectiveness of such lamps.

The production of rare-gas tubes for lighting and display purposes will not be given because the techniques involved are similar to the procedure given for the production of the mercury ultraviolet lamp.

In general, according to F. P. Gross, Jr.,²¹ lighting tubes are classified as follows:

1. Negative glow lamps. The two electrodes of these lamps are close together and light is emitted from the gas around the cathode.
2. Positive column lamps. The electrodes are far apart and light is emitted from the excited gas molecules between the two electrodes.

Each of these two classes of lamps can be subdivided further into hot- and cold-cathode lamps. The hot-cathode lamps operate at lower voltages.

The colors that can be obtained in display lamps depend upon the gas and glass tubing used. Various shades of green are obtained by the combination of yellow glass and mercury vapor. The rare-gas color chart is given in Table 21. The glasses in Table 21 are supplied by the Corning Glass Works. Gas mixtures refer to the code number of Linde Air Products Company.

A more recent development in rare-gas discharge tubes is the fluorescent lamp. These lamps are produced by coating the inner walls of the tube with chemicals (called "phosphors") which will emit visible light when they are sub-



Fig. 153



Fig. 154

jected to ultraviolet radiation. The color range of several are given in Table 22.

TABLE 22.
COLORS PRODUCED BY FLUORESCENT COATINGS

<i>Phosphors</i>	<i>Coating Color</i>
Calcium tungstate	Blue
Magnesium tungstate	Blue-White
Zinc silicate	Green
Zinc beryllium silicate	Yellow-White
Calcium silicate	Yellow-Pink
Cadmium borate	Pink

The color chart for fluorescent lamps is given in Table 23.

TABLE 23. FLUORESCENT LAMP COLOR CHART

<i>Color</i>	<i>Gas</i>	<i>Pressure mm. Mercury</i>		<i>Glass</i>	<i>Coating Color</i>
Rose Pink	Neon	10-18	No	Clear	Blue
Gold	Neon-argon mixture	10-18	Yes	Noviol	Yellow
Yellow	Neon	10-18	No	Clear	Green
Green	Neon-argon mixture	10-20	Yes	Clear	Green
Blue	Neon-argon mixture	10-20	Yes	Clear	Blue
White	Neon-argon mixture	10-20	Yes	Clear	White

THE KINETIC VACUUM SYSTEM FOR EQUIPMENT PRODUCTION

Kinetic systems were previously defined as systems in which vacuum is maintained by virtue of high-speed condensation and mechanical oil pumps. Seals as ground glass-to-glass or glass-to-metal on the high-vacuum side are required, and even though the leakage from such joints may be appreciable, it must not be to the extent that the desired vacuum cannot be maintained. In other applications of the kinetic vacuum system, the high-speed pumps are necessary, because of the degassing that is obtained from the materials in the system as in the case of molecular distillation.

Metallizing of Glass

The use of the kinetic system for equipment production is important in the metallizing of glass. Considerable work in recent years has shown that this process has many applications. Aluminum is one of the metals that can be successfully evaporated. The most practical method of evaporating this metal is by the procedure outlined by J. Strong.^{22, 23} A tungsten filament is used. Tests²⁴ have shown that only about 3% (volume) of tungsten is found in molten aluminum samples when the latter is fused on a tungsten filament. It was also shown that very little tungsten is evaporated, for only 0.03% was found in the aluminum on the glass surface. Actual photographs²⁵ of the filament during the evaporation process have also shown that the aluminum is evaporated from the tungsten filament

adjacent to the molten aluminum, rather than from the molten surface of this metal.

Since mirrors, either opaque or partial, are used in equipment, it will be helpful to outline briefly the procedure for coating glass surfaces with aluminum. It should be pointed out that sometimes considerable experimentation is required before the correct techniques are mastered. A discussion of the vacuum system, glass cleaning and coating techniques will be given as an application of the kinetic vacuum system in equipment production.

The size of the system to be used for metallizing glass surfaces will depend on the size of mirrors to be produced. Small and comparatively inexpensive systems can be built from equipment on hand in the laboratory. Several commercial suppliers (among them Distillation Products, Inc., of Rochester, N. Y., and National Research Corp., of Boston, Mass.) have complete units which can be purchased if it is desirable to set up a permanent metallizing system. A small and simple system can be built with the following equipment:

1. A 12" glass bell jar with a metal base fitted with a 1" vacuum outlet, four insulated and vacuum-tight electrical binding posts, four filament supports, a mirror support and an adjustable shield which can be used to blank out the filament from the mirror. This shield can be supported with a pulley arrangement with an iron counterweight. A permanent magnet is used for lifting the shield prior to the metal evaporation step.

2. Two large cold traps.

3. A mercury or oil condensation pump, with a speed of about 10 to 20 liters sec. at 0.001 mm. of mercury.

4. A mechanical oil pump, its speed matched with that of the condensation pump.

5. A McLeod gage.

6. A 500-watt transformer with four voltage steps from 4 to 24 volts.

7. An ammeter with a 0-30 ampere range.

8. A voltage transformer. The General Radio Co.'s "Variac" 0-130 volts, rated at 500 watts, is satisfactory.

Arrangement of Vacuum System.—The metal base to the bell jar is anchored to the top of a small table. The vacuum outlet, a 1" Kovar tube, is welded into the metal bell jar base after the glass-to-Kovar seal is made. This line extends through the top of the table. The electrical lines which are connected to the binding posts also extend through the table. A glass cold trap is sealed to the high-vacuum side of the condensation pump. A line to the McLeod gage is sealed into this connecting vacuum line. A bleeder line with a 3 mm. bore stopcock is also sealed to this line. The outlet of the mercury condensation pump is connected to the mechanical

pump through a second cold trap. This arrangement of bell jar, cold trap, condensation and mechanical pumps can also have a line which by-passes the condensation pump, i.e., a line from the cold trap below the bell jar to the mechanical pump. Large stopcocks (10-mm. bore) are then required to isolate the condensation pump during the initial evacuation and to close the by-pass line when the mercury condensation pump is started.

If an oil condensation pump is used, the liquid nitrogen cold traps are not necessary and the pump can be connected directly to the vacuum outlet line of the bell jar base. In this case it is also convenient to have the McLeod gage and the bleeder lines connected directly through the metal base of the bell jar.

The Tungsten Filament.—The 20-mil tungsten wire should not be brittle. When the filament is purchased it should be specified that the wire should be soft enough so that it can be wrapped around its own diameter. The location of the filament coil or loops containing the aluminum will depend on the size and shape of the proposed mirror backing. P. Bonet-Maury²⁶ found that when polonium was evaporated in high vacuum, it condensed on a plane surface in an amount proportional to the inverse square of the distance from the evaporation point. J. Strong²⁷ assumed that other metals behaved in the same way and gave the following equation for film thickness when metal is evaporated from a point source to a plane surface:

$$\tau_P = \frac{m}{4\pi dr^2} \cos \theta \quad . . . \quad 27$$

where τ_P = the film thickness

m = mass of metal evaporated

d = the density of the metal

r = distance from source to the condensation surface

θ = inclination angle

The evaporation points can be so arranged that a uniform aluminum film thickness can be obtained on the mirror base. This is especially desirable when partial mirrors are produced. Filament spacing for the production of circular mirrors is given by J. Strong.²⁷

Cleaning Glass. — The two essentials for preparing the glass for aluminizing are that it must be *clean* and *dry*. Procedures for cleaning glass have been given by J. Strong²⁸ and V. Vaud.²⁹ A satisfactory method used in this laboratory is as follows:

1. The glass is thoroughly washed in a solution of distilled water and the commercial detergent "Dreft."
2. The glass is cleaned by dipping it into cleaning solution (sodium bichromate dissolved in sulphuric acid), then rinsed with distilled water.

3. The glass is then rubbed with a cotton swab which has been dipped into a mixture of a 1% solution of Aerosol OT and precipitated chalk. Optically-ground surfaces should not be treated in this manner because of the possibility of scratching the glass surface.

4. Step No. 2 is repeated and the glass is left in distilled water (not more than an hour). It is important not to pile the glass pieces on top of one another while they are in the water.

5. The glass is washed in two successive baths of absolute ethyl alcohol. It is dried with lens tissue or a silk handkerchief which has been rinsed in chemically pure benzene and completely dried.

Production of Opaque Mirrors. — Opaque mirrors are made as follows:

1. The point source or sources for the evaporation of aluminum will depend on the size and shape of the glass which is to be coated. Calculations for aluminum film thickness can be made by using equation 27. The evaporation sources can then be located from the calculated results.

2. The tungsten filament is cleaned with crocus cloth and small loops are bent in the filament at the required points. The filament is then fastened to the filament holders by small set screws.

3. Aluminum foil, sufficient to give the required film thickness, is then folded over the loops in the tungsten filament.

4. The clean and dry glass is placed on the holder and the shield is placed over the glass. The glass bell jar is then set into position and the outside edges of this jar are sealed with Apiezon grease No. Q.

5. The system is then evacuated with the mechanical pump until the pressure is 0.01 mm. of mercury. The cold traps are then partly immersed in liquid nitrogen and the condensation pump is started. The system is pumped until the pressure is 10^{-5} mm. of mercury. The cold traps are then totally immersed.

6. The aluminum foil is fused to the tungsten filament while the shield is over the glass. The voltage transformer is turned up slowly in this operation until the ammeter reads 10 amperes.

7. The shield is then removed by lowering the iron counterbalance with a permanent magnet. The filament is then flashed at 12 to 18 amperes from 10 to 30 seconds.

8. The vacuum is broken by slowly opening the bleeder stopcock after the condensation and mechanical pumps are stopped.

Partial Mirrors.—Partial mirrors, which reflect as well as transmit light, are used in interferometers and certain

other optical systems. These mirrors are made by controlling the amount of aluminum which is deposited on the mirror base. In this case it is even more important to locate the evaporation point sources. This can be done by calculation as outlined in the production of opaque mirrors. An outline for the production of partial mirrors is as follows:

1. The filament is fastened to the filament supports. The filament loop or loops are located according to the above calculations.

2. Aluminum foil, 5 mm. square, is then placed on the filament loops. The bell jar is closed and the system is evacuated until the pressure of 10^{-5} mm. of mercury is obtained.

3. The aluminum is then completely evaporated from the tungsten filament. If the filament is watched in the operation, it will be possible to see when the aluminum is all evaporated because the filament will also begin to glow at the point where the aluminum was located.

4. The vacuum is then broken and the bell jar is removed. The clean and dry mirror base is placed on the holder and the weighed amount of aluminum is placed on the filament loops.

5. The bell jar is then replaced, sealed and the system is evacuated.

6. The aluminum is then evaporated to the mirror base.

It is very difficult to reproduce partial mirrors. If sufficient data are accumulated on reflectivity or transmission obtained from evaporating different weighed amounts of aluminum, it is not difficult to reproduce mirror transmission within 5 percent.

The oxidation of the aluminum film will also change the characteristics of the partial mirror. Mirrors which give a transmission of 16% to 18% and 43% to 45% when first produced, will give a transmission of 20% and 50% respectively, after the aluminum film is oxidized.

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GAS ADSORPTION APPARATUS FOR MEASURING
SURFACE AREAS

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Research]

In recent years the study of the adsorption of gases on solids has received considerable attention from both the theoretical and applied scientist. This is due in a great part to the excellent work of Brunauer, Emmett and Teller¹. They showed how the total area of a porous or finely divided powder could be calculated from gas adsorption data. Because of the increasing importance of this type of work, this article will be devoted to a description of the most general form of gas adsorption apparatus. Details of the operation and method of obtaining the surface area will be included.

The surface area of a solid is of extreme importance in many chemical processes where gas or liquid reactions occur either on the surface or under the influence of the surface of solids. Contact catalytic reactions, such as take place in the cracking of hydrocarbons, the hydrogenation of vegetable oils and adsorption refining processes such as occur in clay treating of gasolines and in sugar refining are a few cases where surface area is important. Since most of the solids which are used as catalysts or adsorbents in this type of work are of a porous nature an adequate measure of the surface area must include the area involved in the walls of the pores (the internal area) as well as the external area. Indeed in most cases the internal area is many times greater than the external and is generally the more important of the two.

The problem in measuring the total surface area of such porous substances is to find a unit of measurement of area small enough to be used in the sub-microscopic pores which may be only a few Ångstrom units in diameter. The molecules of a gas such as nitrogen prove to be a suitable yardstick and have the advantage that we know or can estimate their size with a reasonable degree of accuracy. If one could completely cover the surface of a solid including the internal area with a single layer of gas molecules (e.g. nitrogen) and then count the number of molecules it took to do so it would be possible to determine the total area since the area covered by a single molecule can be determined from known physical constants of the gas. This is essentially the procedure developed by Brunauer, Emmett

and Teller¹ who will hereafter be referred to as BET. They showed how to count the number of molecules of a gas corresponding to a single layer covering the entire surface of a solid.

When a solid is exposed to a gas a definite amount of the gas will adhere to or be adsorbed on the surface of the solid if the temperature is in the neighborhood of the normal boiling point of the gas. This adsorption is due to forces similar to those which are involved in the condensation from the gaseous to the liquid state. The volume of gas which will be adsorbed on any given surface depends upon both the temperature and the pressure of the gas. As the temperature is increased, the amount of gas adsorbed decreases. On the other hand the effect of an increase in pressure is to increase the adsorption. In the determination of the area the temperature is kept constant and the amount of gas adsorbed is measured as the pressure is altered. A plot of such data is called an adsorption isotherm. Although the study of adsorption phenomena in general is extremely important, for the purpose of this article we will consider only the adsorption of nitrogen at temperatures close to its normal boiling point ($-195.8^{\circ}\text{C}.$) since this is the gas most generally used for area measurement. A typical nitrogen isotherm is shown in Fig. 155.

Adsorption isotherms have been classified into five general types but the "S" shaped isotherm shown in Fig. 155 is by far the most common type and the one to which the BET theory in its simplest form applies. (For a more detailed study of the types of isotherms one may consult "The Adsorption of Gases and Vapors, Vol. I, Chapter VI by S. Brunauer). Although many attempts to explain adsorption phenomena have been made, it was not until BET developed the so-called "multilayer theory" that a satisfactory explanation of all five types of adsorption isotherms was possible. The basic assumption of the BET theory is that several layers of gas can be adsorbed on a solid surface. The BET theory results in the following expression for the isotherm of a gas adsorbed on a free surface.

$$V = \frac{V_m cP}{(P_0 - P) (1 + (c-1) P/P_0)} \quad (28)$$

where V is the volume of gas at $0^{\circ}\text{C}.$ and 1 atmosphere pressure, P is the pressure, P_0 is the vapor pressure of the gas at the temperature of the adsorbent, c is a constant related to the heat of adsorption and V_m is the volume of gas (s.t.p.) necessary to form a single layer over the entire surface. It is the determination of the constant V_m which makes possible the measurement of the total area.

Although equation (28) was derived for a flat surface it is still applicable over a limited range to porous materials which have typical "C" shaped isotherms. For certain extreme types of "S" shaped isotherms a more complicated form of equation (28) becomes necessary².

Of the various quantities in equation (28) P , P_0 and V are determined experimentally and V_m and c can be obtained by putting equation (28) into linear form

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} P/P_0 \quad (29)$$

and plotting $P/[V(P_0 - P)]$ vs P/P_0 . If equation (28) is valid such a plot should give a straight line with

$$\text{slope (s)} = \frac{c-1}{V_m c} \text{ and intercept (I)} = \frac{1}{V_m c} \quad (30)$$

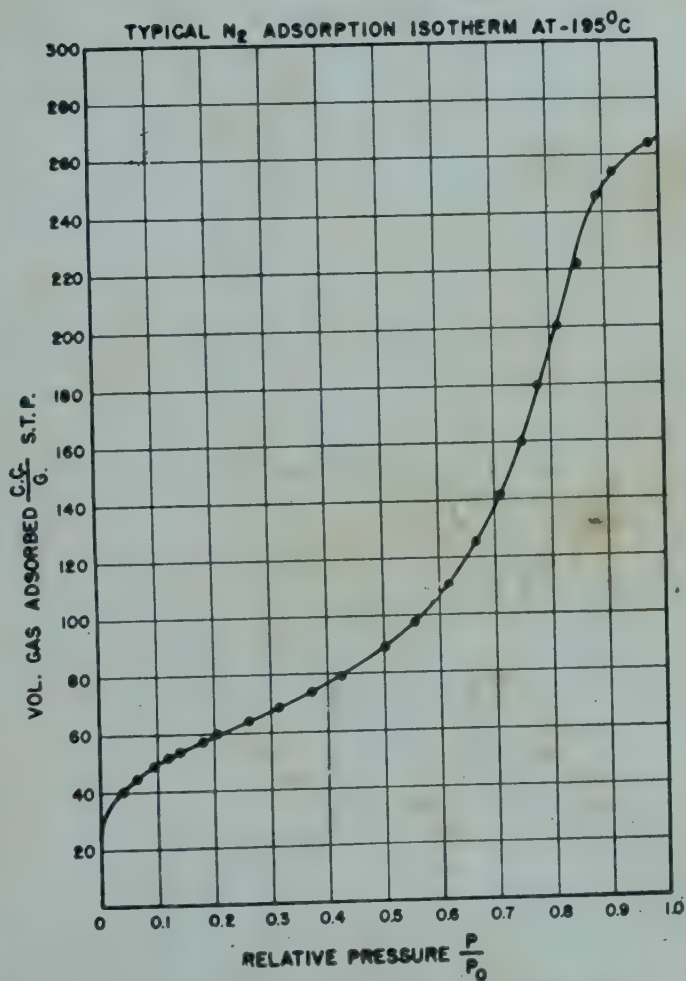


Fig. 155

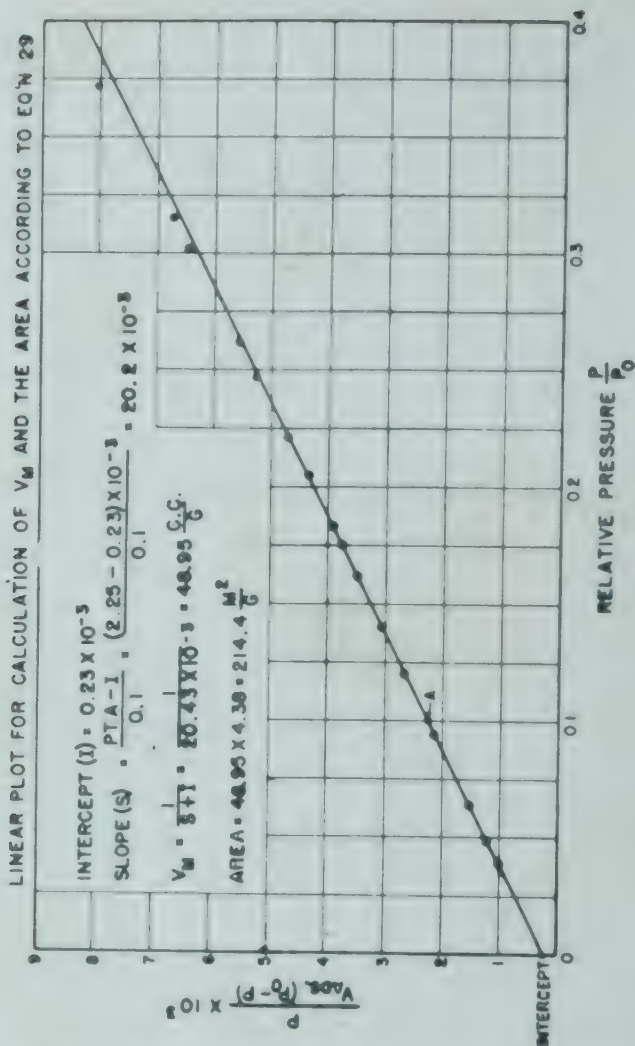


Fig. 156

For most isotherms a straight line is obtained for only the lower portion of the isotherm up to a relative pressure (P/P_0) of about 0.3. This straight line, however, is sufficient to determine the constants V_m and c from its slope and intercept. From equations (30) it is easy to show that

$$V_m = \frac{1}{s+1} \text{ and } c = \frac{s}{I} + 1 \quad (31)$$

Fig. 156 shows the isotherm of Fig. 155 plotted according to equation (29).

Since V_m is the volume of gas at 0°C . and one atmosphere necessary to cover the surface with one layer of gas it is a simple matter to convert it to the number of molecules involved. A detailed discussion of the various assumptions in-

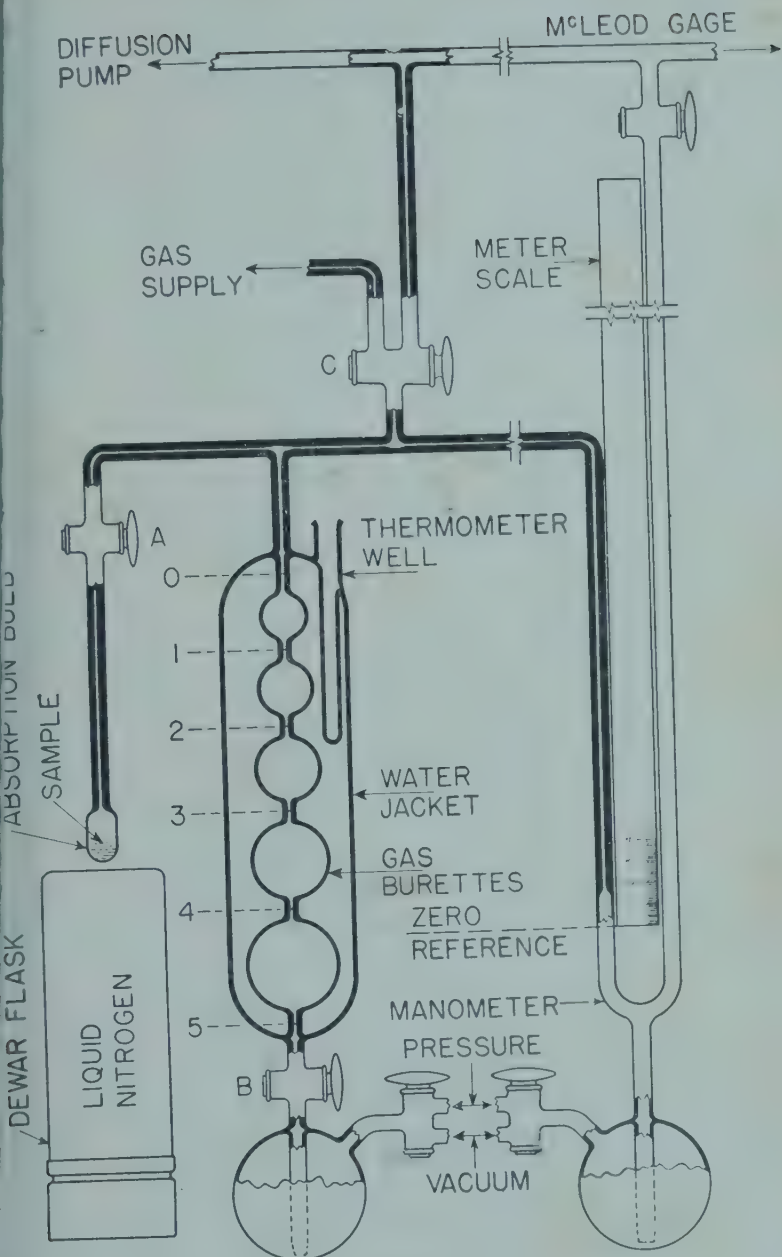


Fig. 157

involved in the determination of the area covered by each molecule is not in place here. Such a discussion is given by BET¹. The end result shows that the total surface area is related to V_m as follows:

$$\text{Area (sq. meters)} = 4.38 V_m \text{ (cc.s.t.p.)} \quad (32)$$

DESCRIPTION OF THE APPARATUS

Having developed a brief outline of the theory it is now necessary to consider an apparatus which will give the experimental data necessary to determine the surface area of a porous or finely divided solid. The type of apparatus discussed here is not the only kind which will give suitable data but it is one of the most common types. The essential parts of the apparatus and its manipulation will be described first. In addition it will be helpful to describe some auxiliary apparatus that may be incorporated into the system in order either to increase the precision and accuracy of the data or to increase the ease of manipulation.

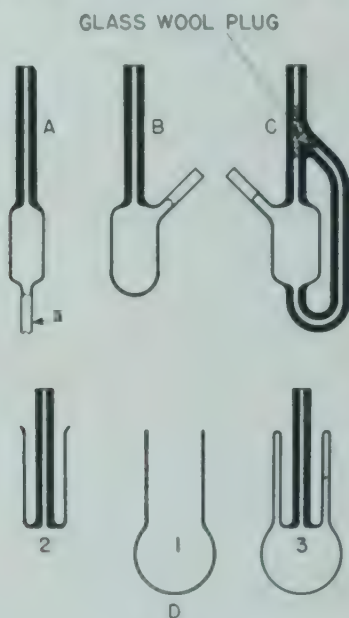


Fig. 158

First, however, it will be helpful to consider what is expected of the apparatus. In order to determine the area utilizing the BET theory, we must have the data necessary to make a plot similar to Fig. 156 in which $P/[V(P_0 - P)]$ is plotted against P/P_0 . Consequently the quantities needed to determine a particular point are P the pressure, V the volume of gas adsorbed at the pressure P , and P_0 the vapor pressure of the gas at the temperature at which the adsorption is being determined. Since several points are required the apparatus should be capable of altering the pressure so that a series of points can be determined without too much difficulty. Inasmuch as P_0 will depend solely upon the temperature of the low temperature bath, it can be determined independently of the actual adsorption data, i.e. P and V .

The common form of low-temperature adsorption apparatus shown in Fig. 157 meets all the requirements outlined above. The volumes of the various bulbs in the burette are determined before the apparatus is assembled. The remaining volume of the system between the zero of the manometer and the stopcock *A* is calibrated as will be described later. The volume of the free space in the adsorption bulb is determined by calibration with helium at the temperature of liquid nitrogen. Helium is used because its adsorption at liquid nitrogen temperature is effectively zero on nearly all solids. Once the volume of all parts of the apparatus is known and the system evacuated, a sample of nitrogen can be admitted to the burette with stopcock *A* closed. By determining the pressure and the temperature of the burette this volume can be converted to standard conditions. With the liquid nitrogen bath surrounding the adsorption bulb, stopcock *A* is then opened. After allowing sufficient time for equilibrium to be established, the pressure is again determined. This, together with the known volume of the system up to stopcock *A*, allows the determination of the volume of gas remaining in the burette. The calibration of the adsorption bulb permits one to calculate the amount of gas in the adsorption bulb. Thus the volume of gas adsorbed is the original volume taken minus the amount remaining in the burette and the amount in the adsorption bulb. By allowing the mercury to fill the various bulbs of the burette the volume of the system can be altered by known amounts and hence several points can be taken in succession without any difficulty.

As indicated in Fig. 157, some auxiliary apparatus is required such as the high vacuum system, gas reservoirs, etc. Since vacuum pumps and gages have previously been discussed, they will not be mentioned except to point out that they are needed. The details on the rest of the system will now be discussed.

Gas Reservoirs

Two gas reservoirs of 2- to 5-liter capacity are required; one for the helium to be used in the calibrations and one for the adsorbate which we will assume to be nitrogen. They should be attached to the system in such a way that they can be completely evacuated before being filled with the gas. It is good practice to keep the pressure in the reservoirs always above atmospheric so that there will be no danger of air leaking into the reservoir through a faulty stopcock. Care must be taken not to have the pressure so high that the stopcocks are blown loose. Pressure stopcocks are recommended. An open end manometer at least 76.0 cm. long attached to the reservoir is convenient for determining

the amount of gas in the reservoir. A more complicated type of reservoir but one which has certain advantages and can be used for storing gas at subatmospheric pressures will be described later in connection with a more elaborate apparatus.

Manometer

Since it is necessary to keep the volume of the system constant, the mercury in the pressure leg of the manometer is always adjusted to a reference point corresponding to the zero point of the scale. The manometer should be made of 10-mm. tubing so as to minimize meniscus effects of the mercury. In order to avoid capillary effects the manometer at the reference point must have the same diameter as the opposite leg. The reference point should, however, be as close to the capillary tubing as possible and still have the proper diameter, otherwise the free space of the system will be needlessly increased. The manometer should also extend for several inches below the reference point so as to avoid the danger of the mercury being accidentally forced around the "U" bend during a rapid increase in pressure.

Burette

The burette, Fig. 157, consists of a series of bulbs of various sizes connected by short lengths of capillary tubing. Some type of reference mark is made on each capillary tube and also below the bottom bulb and above the top bulb. In this way each bulb has a reference mark above and below it and the volume between the marks for each bulb must be accurately known. These volumes are determined by calibrating with water or mercury before the burette is attached to the system. In order to calibrate the burette the stopcock *B* should be attached. By means of a vacuum pump attached to the upper capillary, mercury may be drawn up into the burette filling all the bulbs up to the top reference point. The flow of mercury is, of course, controlled by the stopcock. The temperature of the burette is then taken. A tared beaker is placed under the stopcock which is then opened until the mercury drops to the second reference mark. The volume of mercury collected in the beaker will correspond to the volume of the top bulb. The mercury collected is then weighed and from the density of mercury at the temperature of measurement, the volume of the bulb corrected to 0°C. will then be

$$\text{Vol. (cc.)} = \text{weight (gm.)} / d \text{ (gm./cc.)}.$$

Since most of the gas volume in the system is in the burette bulbs, it is important that the burette be thermostated. This may be accomplished simply by a water jacket with an air jet for agitation or liquid from a constant tem-

perature bath may be circulated through the jacket. In either case the temperature should be known accurately to at least 0.1°C .

The size of the various bulbs of the burette is not too important. A convenient range of volumes is 5, 15, 25, 50, 130 cc. If the volumes are too large the pressure increments will be large and the various readings may be too far apart for accuracy. On the other hand small burette volumes make it difficult to cover a reasonable range of pressures.

Adsorption Bulb

This is the container which holds the sample of adsorbent. There is no set design for such a bulb and the type used may vary according to the nature of the adsorbent. The principal requirements are low free space, i.e. no larger than necessary to hold the sample, and ease of construction. Several types are shown in Fig. 158. The simplest and the most convenient bulbs for most ordinary adsorbents are shown in Fig. 158, A and B. The adsorbent is introduced through the tube "a" which is then sealed off. The container, Fig. 158, C, is useful when the adsorbent is very finely divided. The two outlets decrease the rate of flow of gas and the glass fiber plugs stop the adsorbent from being blown out of the bulb during the degassing process. This is an important advantage for materials such as "fluid" cracking catalysts. The bulb, Fig. 158, D, is used when the adsorbent is of such a nature that it cannot be heated. The bulb is made in two parts, 1 and 2. The sample is placed in the bottom of 1. The bulb, 2, is then placed inside of 1 and the final seal made around the upper rim at 3. This seal is far enough away from the sample to avoid excess heating of the sample and yet the completed bulb has a minimum of free space.

The size of the adsorption bulb depends upon the adsorbent. It has been found that for most porous substances 0.2 to 0.5 gm. is a convenient sample size. For substances which are non-porous or which have small specific areas larger samples should be used.

Bath, Furnace and Thermometer

Besides the above-mentioned parts of the system there are three pieces of equipment that are essential; the liquid nitrogen bath which is used to keep the adsorbent at the proper temperature, a sensitive thermometer to measure the temperature of the bath and a furnace suitable for heating the adsorption bulb and sample while it is being evacuated.

Since the bath is to hold liquid nitrogen at -197°C . it is necessary that it be of the Dewar type. It has been found that a 665-cc. wide-mouth "Thermos" jar is the most convenient bath. Liquid nitrogen has a tendency to stratify

thermally but a slow stream of nitrogen gas bubbled through the bath will agitate it and keep the temperature uniform. Since the temperature of liquid nitrogen is below the temperature at which oxygen condenses, the oxygen in the air condenses into the liquid causing the temperature to increase slowly. The nitrogen agitator decreases this effect since it keeps a layer of nitrogen gas over the liquid. A loose-fitting cover with holes to admit the adsorption bulb and thermometer is effective in keeping the temperature constant. The tendency of liquid nitrogen to condense oxygen is a potential source of danger. Upon standing the liquid becomes oxygen-rich. In cases where the bath has been used all day and then allowed to stand overnight, the residue which remains the next morning may be almost pure oxygen. Liquid oxygen must of course be kept out of contact with organic materials.

Since P_0 , the vapor pressure of nitrogen at the temperature of the adsorption (approx. $-195^{\circ}\text{C}.$) is needed, it is most conveniently obtained from vapor pressure-temperature tables such as those given by Farkas and Melville³. Thus it is necessary to know the temperature of the bath accurately. Since the vapor pressure of nitrogen varies from 922 mm. at $-194^{\circ}\text{C}.$ to 833 mm. at $-195^{\circ}\text{C}.$, in order to know P_0 to the nearest millimeter, the temperature must be known to at least $0.01^{\circ}\text{C}.$ This can be done with a good thermopile (at least ten junctions) and a potentiometer capable of measuring differences of a microvolt. A less expensive apparatus is an oxygen vapor pressure thermometer. The construction and technique of filling an O_2 thermometer is very well described in Farkas and Melville³. A good source of pure oxygen is a 250-cc. bulb one-quarter full of C.P. potassium permanganate and sealed to a 1" tube 10" long filled with glass wool and connected through a stopcock to the thermometer. This should of course be evacuated with the rest of the system. A brush flame will easily decompose the KMnO_4 giving off very pure oxygen. KMnO_4 decomposes at $240^{\circ}\text{C}.$ The thermometer must be mounted in such a way that it can be removed from its position beside the adsorption bulb whenever the adsorption bulb is being degassed in the furnace. A hinged rack or movable stand will accomplish this very conveniently.

The final piece of equipment is a furnace for degassing the sample. Since most porous materials adsorb gases which may be held more or less firmly to the surface, simple evacuation is seldom sufficient to remove all the adsorbed gases. To completely free the surface of all adsorbed molecules may require evacuation for many hours at temperatures of $1400^{\circ}\text{C}.$ or higher. Fortunately it is seldom necessary to

go to such extremes when the surface area is to be determined. Unless a solid has been exposed to organic vapors, adsorbed water vapor is the only substance likely to cause trouble. Heating under vacuum to 150° or 200°C. for an hour is generally sufficient to degas most samples. In cases where the solid has been exposed to organic substances such as chloroform, benzene or acetone, it may be necessary to raise the temperature to 400 or 500°C. The most simple type of furnace to make and use is a glass or ceramic tube of sufficient diameter to fit over the adsorption bulb. This ceramic tube is wound with resistance wire and covered with some insulating material. A "Variac" or other voltage control can be used to adjust the temperature of the furnace.

SURFACE AREA DETERMINATION

After the apparatus is assembled it should be completely tested for its capacity to hold a vacuum. It is generally found that a newly-erected system cannot be evacuated to a good vacuum because of adsorbed water vapor on the glass walls of the system. This may be easily removed by heating the glass tubing (being careful not to heat the stopcocks) with a brush flame while the vacuum pumps are in operation.

The next step is to calibrate the free volume of the adsorption system. This is the portion of the system, Fig. 157, between stopcock A, the zero reference of the burette and the zero reference of the manometer. The volumes of the various bulbs are already known by the mercury calibration. To determine the volume of the free space (V_0), with the stopcock A closed and mercury in the manometer, enough gas (either nitrogen or helium) is admitted to the adsorption system to give a pressure of 700 to 800 mm. when the mercury in the burette is at the zero reference. The stopcock to the gas manifold is then closed and the pressure determined with the mercury in the burette on the zero reference. The mercury is then lowered to the No. 1 reference point and the pressure redetermined, this is repeated at the next reference point and so on until all the burette bulbs have been emptied of mercury. We now have a series of pressure readings and we know the total volume of the burettes which were not filled with mercury, V_{tB} , for each pressure reading. Assuming the temperature remained constant during the calibration run and bearing in mind that a constant amount of gas was used throughout we have

$$\begin{aligned} PV &= \text{constant} = K \\ \text{but } V &= V_0 + V_{tB} \\ \text{hence } PV_0 + PV_{tB} &= K \end{aligned} \tag{33}$$

$$\text{or } PV_{\text{TB}} = K - PV_0$$

$$\frac{d(PV_{\text{TB}})}{dP} = -V_0$$

Hence if we plot PV_{TB} vs. P for each point taken, it should give a straight line the slope of which is the negative of the free volume. Since V_{TB} was corrected to 0°C ., V_0 will already be referred to the same temperature. Fig 159 shows such a plot.

We now know the volume of all the parts of the system up to the stopcock A. Rather than having to add up all the

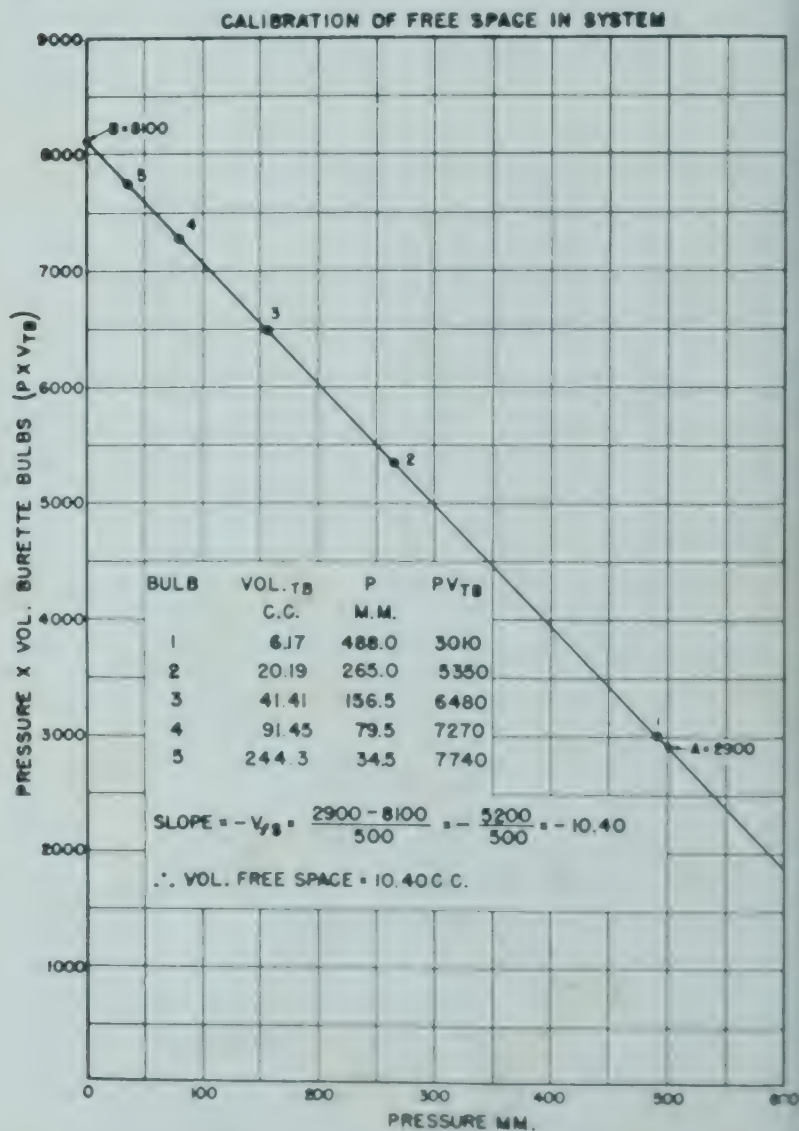


Fig. 159

volumes each time they are used it is convenient to make a table of the volume of the system for each position of the mercury in the burette. Since the gas in the system will always be corrected to s.t.p. it saves time if these volumes are multiplied by 273.2/760. The resulting set of factors will be called volume factors (f_v). Thus for any amount of gas in the system for which the pressure and temperature have been determined

$$V \text{ at s.t.p.} = \frac{f_v \times P}{T} \quad (34)$$

where f_v is taken corresponding to the number of burette bulbs used, T is in degrees absolute.

Once the system is calibrated it is ready for actual adsorption measurements. The adsorption bulb is filled with a weighed amount of the solid under investigation and the stopcocks are set so that the entire system including the adsorption bulb will be evacuated. The furnace is put in place surrounding the adsorption bulb and adjusted to the proper temperature. After the degassing has proceeded for at least an hour and the McLeod gage shows the minimum pressure, the furnace is removed and stopcock *A* closed. After cooling, the liquid nitrogen bath is placed in position so that the adsorption bulb is completely immersed in the liquid.

The free volume of the adsorption bulb must of course be determined, i.e., all the space in the adsorption bulb not occupied by the solid. This volume includes the space contained in the pores of the sample. This can only be done by using a gas which is not adsorbed at the low temperatures of the bath. Helium serves the purpose very well.

To obtain this free space a rather large sample of helium is introduced into the burette system with stopcock *A* still closed. The pressure is measured and the volume of helium is corrected to standard conditions as previously described. This volume is designated as V_T (He). The stopcock *A* is then opened and the helium admitted to the adsorption bulb. The new pressure P_1 is then determined. From P_1 , the temperature of the burette and the corresponding bulb factor the volume of helium remaining in the burette system V_R (He) can be determined. The volume of gas which entered the adsorption bulb when the stopcock was opened is then

$$V_T \text{ (He)} - V_R \text{ (He)} = V_A \text{ (He)} \quad (35)$$

V_A (He) is of course the volume of the gas at s.t.p. since both V_T and V_R were referred to s.t.p. V_A will of course vary with the pressure P_1 . If V_x is designated as the absolute volume of the free space in the adsorption bulb and T_x the temperature of the bath then

$$V_A (\text{He}) = \frac{V_x P_1}{T_x} \frac{273.2}{760} \quad (36)$$

or
$$\frac{V_A (\text{He})}{P_1} = \frac{V_x}{T_x} \frac{273.2}{760} = \text{constant} = f_A$$

Hence by dividing $V_A (\text{He})$ as obtained in equation (35) by the corresponding pressure a constant is obtained. This constant (f_A) may be termed the adsorption bulb factor. Multiplying f_A by the pressure at any time will give the volume of gas corrected to standard conditions contained in the adsorption bulb. The volumes of all parts of the system are now known and the nitrogen adsorption determinations can now be made.

The helium is first pumped out of the system with the nitrogen bath removed. Stopcock *A* is then closed and the bath replaced. A dose of nitrogen is then admitted to the burette system and its volume determined in the usual manner. Let this volume be $V_T (\text{N}_2)$. The size of $V_T (\text{N}_2)$ depends upon the nature and amount of the sample under investigation. The nitrogen is then admitted to the adsorption bulb through the stopcock *A*. As the gas is adsorbed on the surface the pressure will gradually drop. Sufficient time must be allowed for the adsorption to reach equilibrium. When the pressure has reached a constant value it is recorded. The temperature of the burette must also be recorded and the position of the mercury in the burette. The temperature of the cold bath should be recorded for each reading even though it does not change appreciably. If an oxygen vapor pressure thermometer is being used it should be in place in the bath during the entire experiment. This completes the data necessary to determine the first point.

A second point is obtained by moving the mercury in the burette to the next reference point, thereby decreasing the volume of the system with a corresponding rise in pressure. When the adsorption has again reached equilibrium at this new pressure, the data are recorded and the process repeated until the burette has been completely filled with mercury.

To calculate the volume of gas adsorbed, we know $V_T (\text{N}_2)$ and P , T and volume factor (f) for each point taken. We also know P_0 , the vapor pressure of nitrogen at the bath temperature.

$V_T (\text{N}_2)$ = total volume of nitrogen taken

$V_R (\text{N}_2)$ = volume of nitrogen remaining in the burette system up to stopcock *A* = $(P \times f) / T$

$V_A (\text{N}_2)$ = volume of nitrogen in the free space of the adsorption bulb corrected to s.t.p. = $f_A \times P$. Hence the volume of gas adsorbed V_{ads} is the difference between the

amount taken V_T and the amount remaining in the gas phase $V_R + V_A$, that is

$$V_{Ads} = V_T - (V_R + V_A) \quad (37)$$

Equation (37) assumes that nitrogen obeys the ideal gas law. Actually it does not and so a correction must be made to equation (37). This correction can be easily applied by multiplying V_A by $1 + (\alpha P/760)$ where α is a constant depending upon the temperature and the gas used. For nitrogen at -195°C . α is 0.05. For other gases and temperatures Emmett and Brunauer⁴ have listed values of α .

In the plot of the adsorption isotherm it should be noted that the volume adsorbed is plotted against the relative pressure. The relative pressure is simply P/P_0 .

Having calculated the volume adsorbed for each of the points taken the total surface area of the sample may now be determined.

Calculation of the Area

As was pointed out with reference to equation (29), a plot of $P/V (P_0 - P)$ against P/P_0 should give a straight line whenever equation (28) is a valid equation for the isotherm. It has been found from the examination of a great many "S" shaped isotherms that equation (28) does fit the data and hence a plot of equation (29) is linear over the relative pressure range 0.05 to 0.3 or higher. Below and above these limits the data deviate from linearity. The procedure then is to plot the data in the form of equation (29) and select the best linear portion. From the slope and interception of this line V_m can be determined by equation (31) and the area by equation (32).

Since equation (29) seldom holds above a relative pressure of 0.35 it is not necessary to plot the data obtained at higher pressures and unless one is interested in the isotherm for purposes other than the calculation of the area it is not necessary to obtain data above this point. It may be noted that

$$\frac{P}{V (P_0 - P)} = \frac{P/P_0}{V (1 - P/P_0)}$$

which is a more simple function to calculate since P/P_0 must be calculated anyway for the right side of equation (29).

VARIOUS REFINEMENTS

Having described the essential features of a gas adsorption apparatus and discussed its operation, we will now describe certain improvements which, although not essential, will increase either the accuracy of the data or the ease of operation of the apparatus.

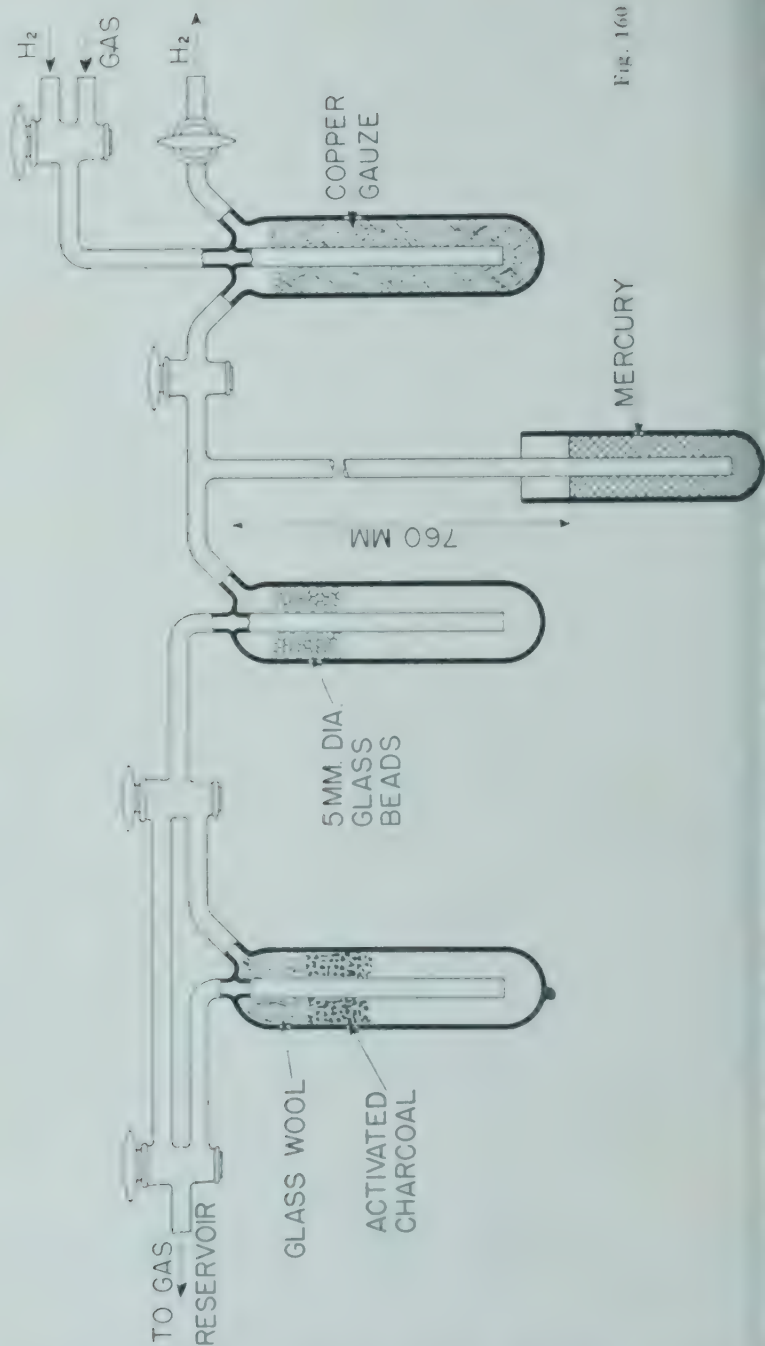


Fig. 160

Since any impurity occurring in either the nitrogen or helium gas used in the apparatus may seriously affect the results, purification of these gases before they are stored in the reservoirs is highly desirable. The most serious impurities that are likely to occur in ordinary tank gases at

moisture and oxygen or, in the case of helium, nitrogen may also be an impurity.

Passing the gas over reduced copper at about 350°C . will remove all but the last few hundredths of a percent of the oxygen*. A trap filled with glass beads and cooled in liquid nitrogen makes a very effective drying tube. All gases but the inert gases may be removed from helium by passing it over activated charcoal also cooled to liquid nitrogen temperatures. A simple flow system which may be attached permanently to the gas inlet tube (see Fig. 157) is shown in Fig. 160. This arrangement permits all parts of the gas train to be evacuated before the gas is introduced. The depth of the relief tube in the mercury regulates the maximum pressure at which the gas may be stored in the reservoir.

Although a simple aspirator pump is perfectly satisfactory for applying vacuum to the mercury reservoirs it is often quite annoying. Attaching a large flask or other vacuum tight vessel of at least 20-liter capacity to the vacuum side is a convenient method of maintaining a vacuum for the mercury system. This vacuum reservoir must of course be periodically pumped. This can be done by either the forepump or a separate pump if one is available. Fig. 161 shows a system where the forepump is being used for this purpose. This arrangement is advantageous because when the system is first being evacuated of air by keeping stopcocks *A* and *B* open, the pressure on both surfaces of the mercury is kept the same. When the system is under high vacuum stopcock *A* should never be open when the tank is being evacuated through *B*. A reduction valve and a petcock bored as shown in Fig. 162 solves the problem of easily changing from atmospheric to higher pressures on the pressure side of the mercury reservoirs.

A second source of error in the apparatus as first described is in the determination of P_0 from the oxygen vapor pressure thermometer. Since this involves three steps, determination of the vapor pressure of the oxygen, plus the need of two tables either or both of which may be in error, two of these steps may be eliminated by measuring the vapor pressure of nitrogen directly. A system for doing this is shown in Fig. 163.

One of the most awkward bits of manipulation and the source of possible error is in the setting of the pressure leg of the manometer on the zero reference point. As the

*In spite of the statement in most books on the subject hot reduced copper will not reduce the oxygen content of a gas below about 0.05%. In fact it is extremely difficult to obtain nitrogen completely free of oxygen. Where the matter is critical, lamp grade nitrogen such as is used for filling incandescent lamps should be used. Ref. Exline, Kramer and Bowman; *Journal Institute of Petroleum*, Vol. 29, 1943, page 301.

apparatus was described this had to be done by adjusting the pressure over the mercury in the reservoir. A fine capillary tube and stopcock attached to the reservoir, through which air can be slowly admitted, enables one to slowly raise the mercury to the reference point. This however has

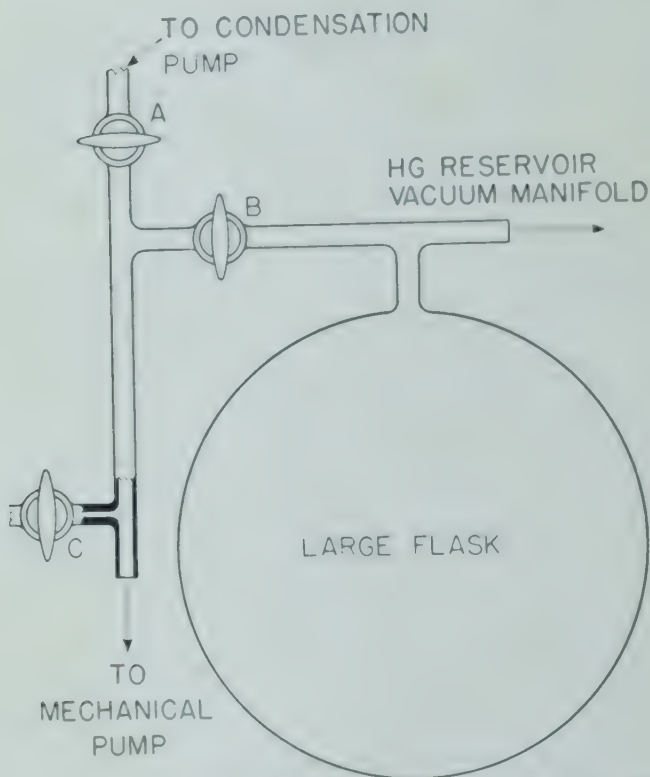


Fig. 161

METAL PETCOCK FOR AIR PRESSURE
ON HG RESERVOIR

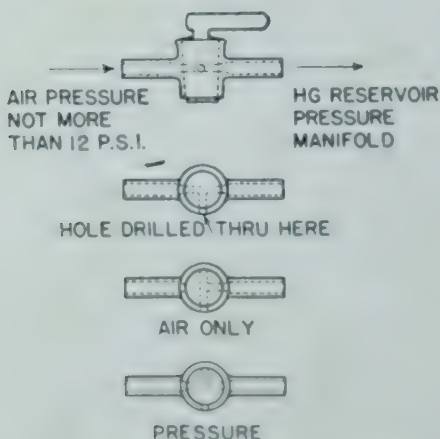


Fig. 162

SYSTEM OF MEASURING VAPOR PRESSURE (P_0) OF GAS DIRECT

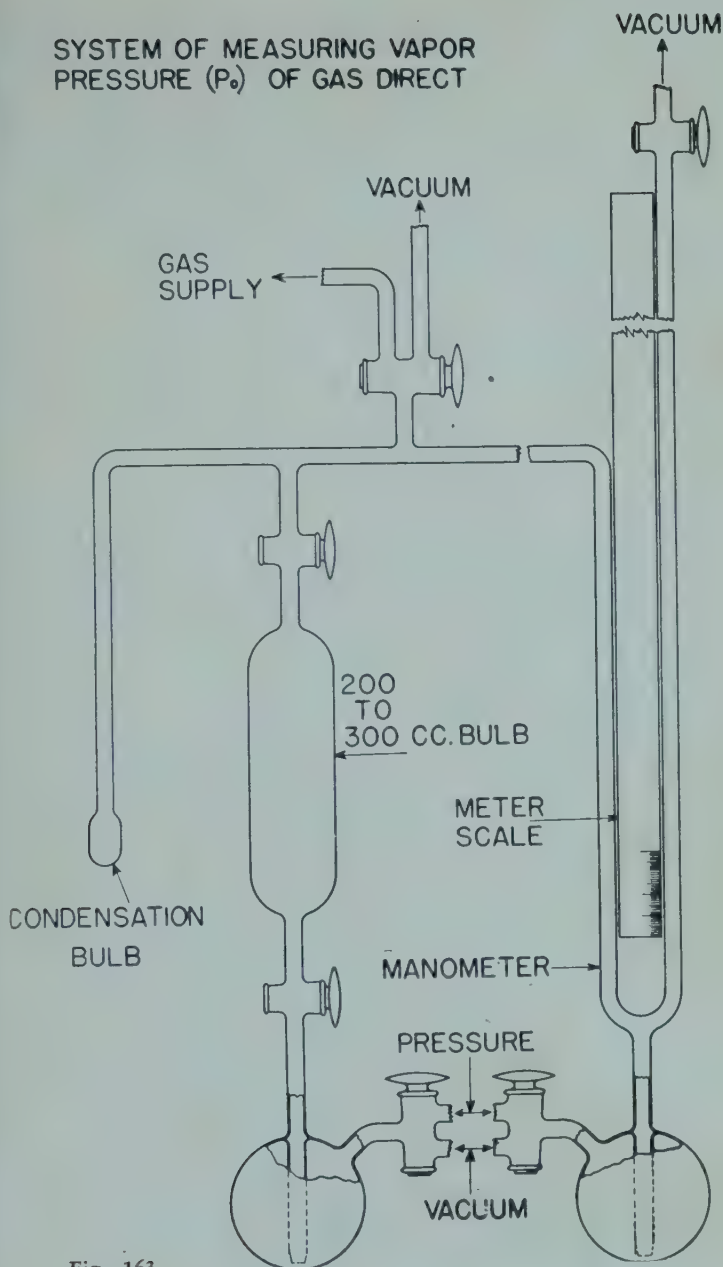


Fig. 163

the disadvantage that it will work only in one direction. The incorporation of two devices solves the entire problem. The first is a fine adjustment control to adjust the mercury level and the second is a contact indicator located at the reference point.

The fine adjustment control is shown in Fig. 164. A side arm is sealed to the reservoir above the mercury level. Six

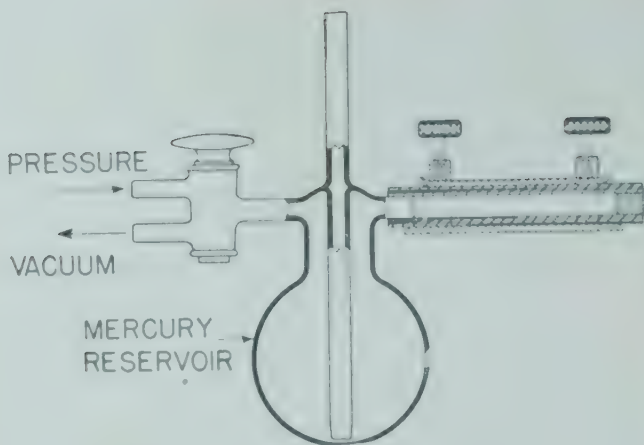


Fig. 164

to eight inches of a medium-weight rubber tubing is attached to side arm so that it extends 5" to 6" beyond the side arm. The open end of the tube is then closed with a rubber plug and sealed so as to be vacuum-tight. By squeezing this rubber tube with a clamp the volume of the air space in the reservoir is altered, with a corresponding small change in the mercury level. Also shown in Fig. 164 is a wide clamp which is useful for squeezing the rubber tube. The operation is simple. With the clamp open the mercury is adjusted roughly to 5 mm. below the reference point by means of the vacuum-pressure stopcock. The stopcock is then closed and the clamp on the rubber tube tightened: this raises the mercury slowly to the reference point. Since by loosening the clamp the mercury can be lowered, it does not matter if the reference point is overshot in the

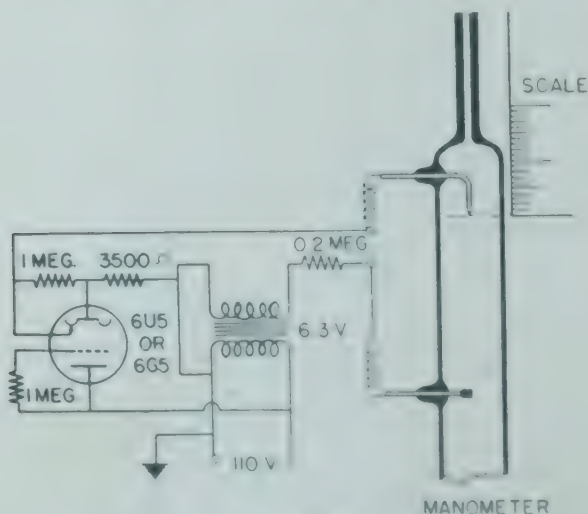
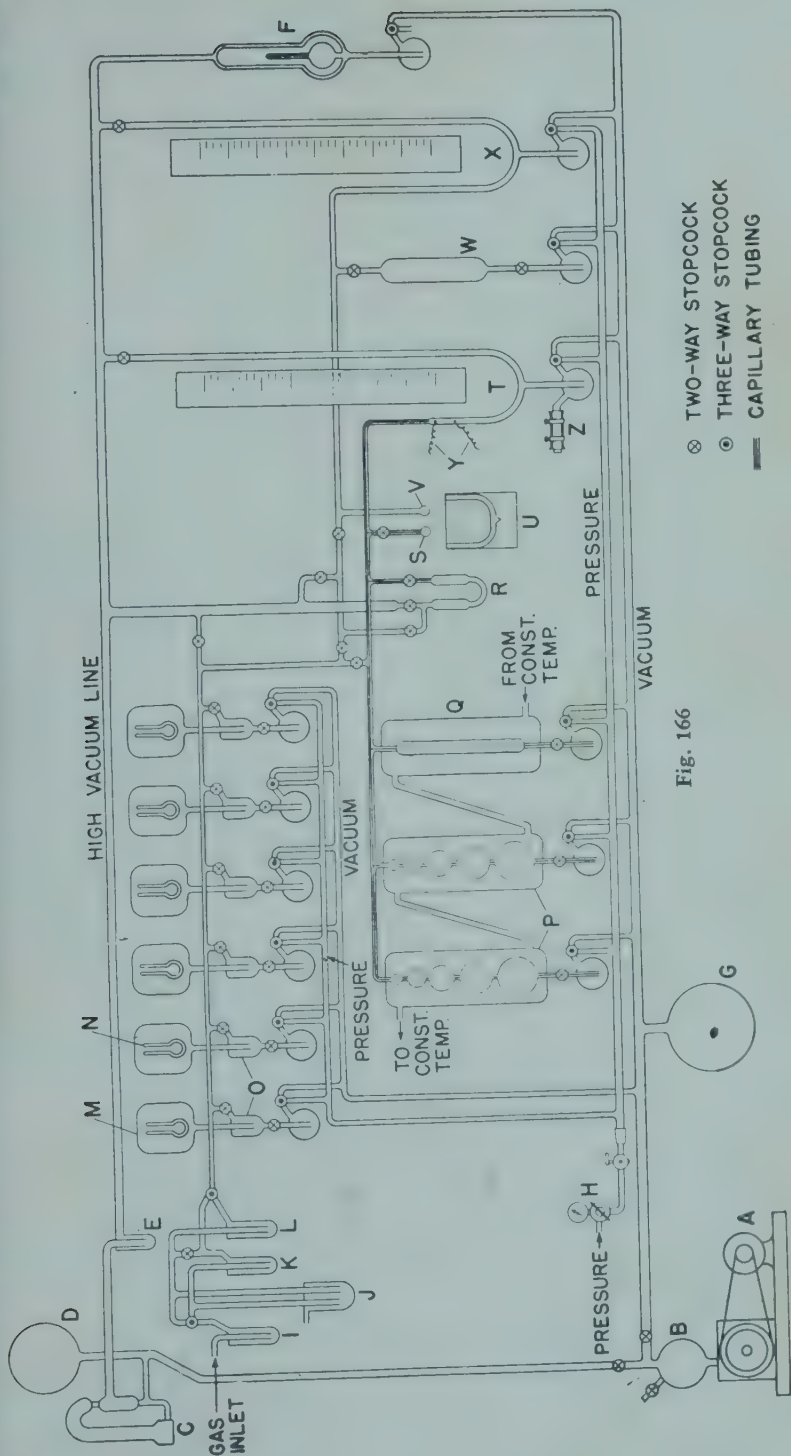


Fig. 165



- ⊗ TWO-WAY STOPCOCK
- ⊙ THREE-WAY STOPCOCK
- CAPILLARY TUBING

Fig. 166

A—Fore Pump	R—Micromanometer
B—Oil Trap	S—Adsorption Bulb
C—Mercury Diffusion Pump	T—Manometer for Adsorption System
D—Fore Vacuum Reservoir	U—Dewar Flask
E—Liquid Nitrogen Trap	V—Vapor-pressure Bulb
F—McLeod Gage	W—Compression Bulb for Vapor Pressure
G—Vacuum Reservoir	X—Vapor Pressure Manometer
H—Pressure Regulator and Petcock Release	Y—Contacts for "Electric Eye" Indicator
I—Trap (Reduced copper turnings—hot) to Remove Oxygen	Z—Fine Adjustment Clamp
J—Overflow Bubbler	A-F—Vacuum System
K—Trap (Glass beads—liquid N ₂) to dry	G-H—Mercury Reservoir Control System
L—Trap (Activated charcoal—liquid N ₂) to Purify Helium	I-O—Gas Purification and Storage
M—Gas Reservoirs	P-U—Adsorption System
N—Indicating Manometers	V-X—Vapor Pressure System
O—Mercury Cut-offs	Y-Z—Devices for Setting Manometer on Zero
P—Bulb Burettes with Constant-temperature Jacket	
Q—Linear Burette (10 ml.)	

first attempt. The success of the device depends upon the rubber tubing used. We have found that tubing $\frac{1}{4}$ " ID, $\frac{1}{8}$ " wall, is most suitable. The rubber should not be too stiff or the adjustment screw will be difficult to operate. Tubing made of gum rubber is probably the best type.

Obviously any error in setting the mercury on the reference point of the manometer causes an error in the pressure reading. A mirror placed in back of the reference mark helps to avoid parallax in setting the position of the mercury. A meter engraved on a mirror makes an excellent manometer. Such a scale can be purchased from the Scientific Glass Apparatus Company. However, any visual reference point is subject to error and it is also a serious strain on the eyes. A simple electrical contact indicator sensitive to 0.01 mm. was described by Mills⁵ and has been used with complete satisfaction. The indicator consists of a tungsten pointer sealed through the manometer and used as the reference point. When mercury touches the pointer it completes a circuit between the pointer and a wire sealed through the manometer wall into the mercury. This circuit operates the grid of an "electric eye" indicator tube. As long as the mercury is out of contact with the pointer, i.e., below the reference point, the eye is open but as soon as contact is made the eye closes. The mercury is considered to be on the reference point when a very slight turn of the fine adjustment control causes the eye to close. Fig. 165 shows a circuit for such an indicator. The pointer can be made by sealing an L-shaped piece of tungsten wire through the wall of the manometer with the point downward as shown in Fig. 165. The point should be as close to the center line of the manometer tube as possible. With continued use the point of the contact occasionally becomes

contaminated. It can be easily cleaned, however, by evacuating the manometer and touching the point of a Tesla coil to the outer end of the contact pointer. The lead wires should first be disconnected so as to avoid damaging the "electric eye" tube.

A gas adsorption apparatus may be used for many purposes other than the determination of the area of a solid, but no attempt has been made to describe such uses or to describe modifications which would adapt the apparatus to particular purposes. To do so would be much too involved for the present purpose. However, an apparatus can be designed to incorporate several features which make it adaptable for various types of adsorption studies. A brief description of some of the features of one such unit used at the Mellon Institute may be of interest.

Since the apparatus was to be a permanent piece of equipment in the laboratory, it was designed so as to have as high a degree of precision as possible. It was desired to have an apparatus which would be capable of measuring both low pressures (0.01 to 1 mm.) and pressures close to the saturation value, i.e., close to P_0 , with as good precision as the intermediate pressure. It was also desirable to utilize gases other than nitrogen. A flow diagram of this apparatus is shown in Fig. 166.

The apparatus was mounted on a rack six feet wide and reaching to the ceiling. The base of the rack consisted of a table 14" high and 34" wide. Two 2" pipes which extended from the table to the ceiling were rigidly fastened at the center of the ends of the table. The cross pieces of the rack consisted of 1" angle iron fastened between the two pipes at intervals of 12". Uprights of $\frac{1}{2}$ " rod were fastened to the cross pieces and at the bottom to the table. All units of the apparatus were then attached to the cross pieces of the rack by using special clamps, Fig. 139. The arrangement of this compact and permanent installation on the rack is shown in Fig. 167.

In order to improve the precision of the pressure readings, a special manometer stand was used with a vernier reader capable of reading to 0.1 mm. This in conjunction with the "electric eye" indicator for the reference point makes very precise pressure readings possible.

To obtain a more detailed adsorption isotherm, it is necessary to make readings at frequent pressure intervals. This requires that a large variety of burette volumes should be available. Consequently a second burette, similar to the one described but with six small bulbs ranging from 5- to 30-cc. capacity, was added to the system. A linear burette of 10-cc. capacity was also used. This burette was made by putting a water jacket on a Pyrex (774) 10-cc. burette (graduated to 0.05 cc.) with the stopcock removed and

capillary tubing sealed to the ends. A calibration reference mark was made on the capillary tubing on the end attached to the adsorption system. When not in use the mercury is always kept at this mark to avoid any volume error that might be caused if one tries to keep the mercury at a point in the wider portion of the burette. The volume between this scratch mark and the first graduation of the burette

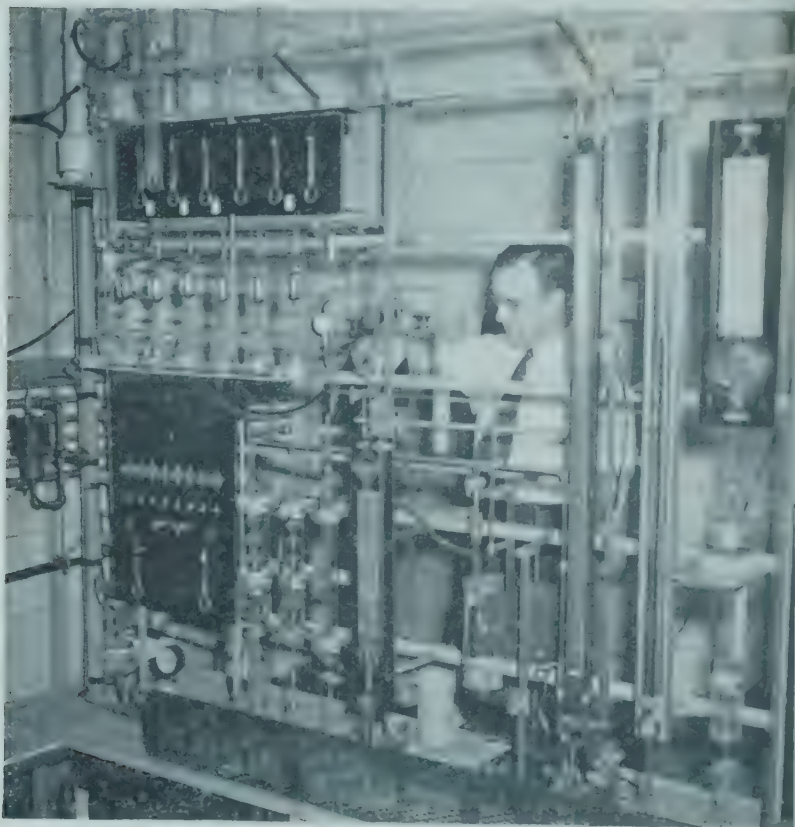


Fig. 167

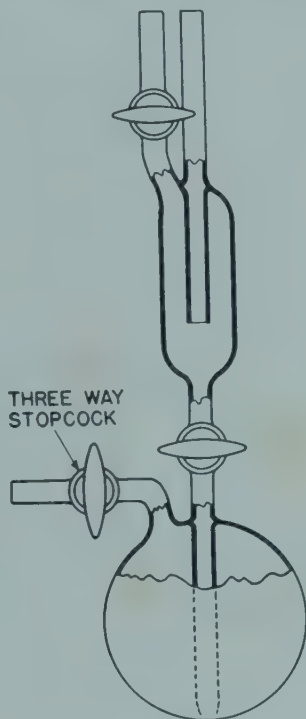
was calibrated with mercury before the burette was attached to the system. The arrangement of the three jacketed burettes is shown in Figs. 166 and 167.

In order to keep the temperature fluctuations at a minimum, liquid from a constant-temperature bath was circulated through all three of the burette jackets.

Since gases other than nitrogen and helium are used for adsorption studies, six gas storage bulbs were incorporated into the apparatus. Some of these gases dissolve readily in the stopcock grease and hence it is necessary to place a mercury cut-off between the storage bulb and the stopcock to the gas manifold of the system. A convenient and suitable type of cut-off is shown in the Fig. 168. When the

cut-off is open the mercury is kept just below the end of the tube from the gas storage bulb. To close it, the mercury is raised in the cut-off up to the upper stopcock which is then closed. In this state there is no possibility of the gas coming into contact with the stopcock nor of air leaking into the storage bulb and contaminating the gas. To open the cut-off again the mercury is lowered. As the mercury drops the pressure in the storage bulb causes the gas to bubble through the mercury into the upper portion of the cut-off. This frees any mercury which may have remained in the short length of tubing below the upper stopcock, if this tubing has a sufficiently large inside diameter. As indi-

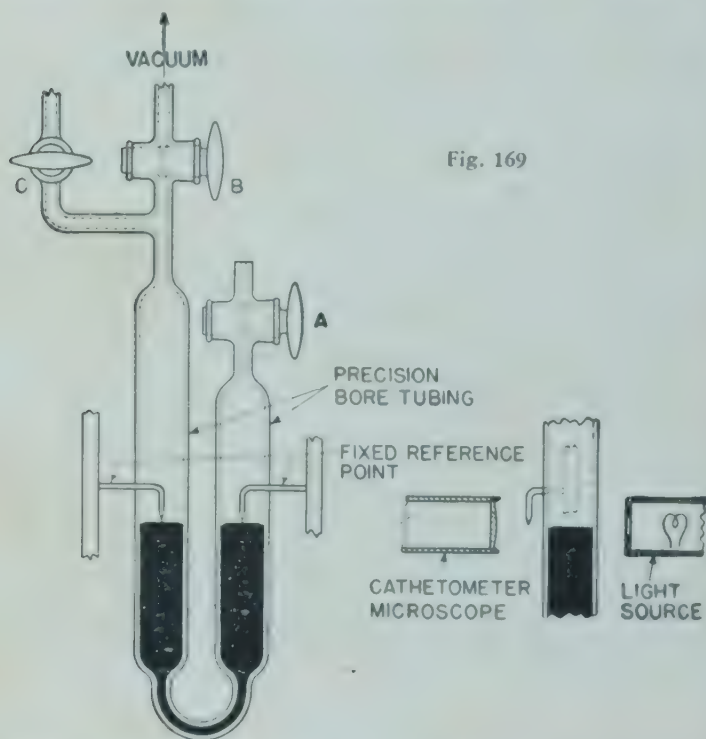
Fig. 168



cated, 8-mm. tubing has been found to work satisfactorily. The location of the mercury cut-off valves is shown in Fig. 166.

With such a cut-off it is perfectly safe to store the gas at pressures of an atmosphere or less since there is no danger of air contamination through a leaky stopcock. This arrangement allows the use of a unique type of manometer only 6" long as an indicator of the amount of gas present in the storage bulb. This is an ordinary 6" closed-end "U" type manometer. Some gas is allowed to remain above the mercury in the closed end. To fill such a manometer, mercury sufficient to half fill the "U" tube is poured into the

open end without evacuation. The excess air trapped in the closed end is then slowly pumped out through the mercury. When as much gas as possible has been pumped out, the vacuum may be released and another half inch of mercury added to the open end of the manometer. The position of the mercury in the closed end should be noted and a mark placed on the glass at this point. This indicates approximately one atmosphere. By pumping on the open end with an ordinary manometer in series with the pump the position of the mercury in the closed end may be noted and marked for various fractions of an atmosphere. The advantage of this type of indicator is that it takes up



much less space than a full-length open-end manometer and consequently may be mounted quite compactly on a panel board as illustrated in Fig. 167. The six indicating manometers were located on the panel above the mercury cut-off valves, Fig. 166.

One of the purposes for which this particular apparatus was designed was to be able to measure accurately pressures as low as 0.01 mm. as well as relative pressures very close to unity. Both of these objectives were attained by using a short large-diameter manometer which is read by means of a sliding microscope cathetometer capable of being read to 0.001 mm. Constant-bore tubing (0.9851" ID) was

used for the two legs of this manometer. Figs. 167 and 169 show how this can be incorporated into the system. To read the low pressures the left arm is opened to the vacuum through stopcock *B* (*C* closed). The difference in the mercury levels then give the pressure directly. To measure pressures close to saturation the left arm is opened through stopcock *C* to the vapor pressure line. Hence the mercury level difference is a measure of $P_0 - P$. P_0 is read from the vapor-pressure manometer and the pressure of the system is determined by the difference.

Since the volume of the right arm of the manometer must be known accurately, the point of a needle fastened to the manometer is used as a reference mark. The volume between the stopcock *A* and this reference point was first determined by the same method as has been described for the determination of the capillary portion of the adsorption system. The mercury was maintained at the reference point by adjusting the pressure in the left side. Since the manometer was made of tubing with a known constant bore, the volume from the reference point to the mercury can be calculated. This value is added to the volume up to the reference point. The use of constant-bore tubing also eliminates any capillary effects on the meniscus if the tubing is perfectly clean.

Although the microscope cathetometer is capable of reading to 0.001 mm., it is hardly possible to read the mercury level this accurately, unless very great care is taken to eliminate all vibration and to use a source of parallel light to illuminate the mercury column.

With an apparatus as complicated as this and which was designed to be of a permanent nature, it was necessary and worth while to have all electrical, water and pressure controls located on a panel board. A sliding stand was designed so that the furnace and liquid nitrogen bath could be moved easily into place about the adsorption bulb without danger to the system. Protecting frames made from $\frac{1}{2}$ " expanded metal were placed about those portions of the apparatus which are in danger of being accidentally broken. All these features were used in the apparatus shown in Fig. 167.

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THE MODIFIED MENZIES-WRIGHT MOLECULAR WEIGHT APPARATUS

[This chapter was prepared in collaboration with Dr. W. E. Hanson, Mellon Institute of Industrial Research.]

The determination of molecular weight is becoming an increasingly common analytical operation. Not only is an exact knowledge of this property important in establishing the structure of or identifying an unknown compound, but it may also serve conveniently to characterize a series of high-boiling cuts in the same manner as the boiling point itself serves for more volatile fractions.

As a specific example, consider the case of a crude oil being separated into narrow cuts by distillation. Throughout the gasoline and kerosene range, fractions are taken according to the boiling point, as this property defines rather narrowly what compounds can possibly be present. As higher boiling material distills, it becomes increasingly difficult and eventually impossible to determine the true boiling temperature. At this point, it is entirely logical to turn to the average molecular weight of the fraction as the basic characterizing property. Until recently, however, this was rarely done, owing to the difficulty and the time required in making satisfactory molecular weight determinations.

As between ebullioscopic and cryoscopic procedure, the latter was generally favored in laboratory work because of its accuracy and its ability to handle materials of widely different volatilities. For substances of higher molecular weight, however, this question of volatility does not enter. Also, because of difficulties attendant upon low solubilities and the tendency for solutes to associate in solvents at their freezing points, several distinct advantages accrue in the use of an ebullioscopic procedure.

The apparatus described below is one which was developed specifically to meet the need for a precise and rapid method for the routine determination of the average molecular weight of heavy petroleum oil fractions. In use it has enjoyed wide application, not only in a variety of routine analytical problems but also in the exacting field of compound structure and identification.

It is basically the same as that described by Hanson and Bowman¹. Two important changes have been made: A radio tube socket is employed to protect the leads to the press seals and an external heater has been substituted for the original heater which was immersed in the solvent.

CONSTRUCTION OF THE APPARATUS

The molecular weight apparatus is not difficult to make. Production of the instrument does require several techniques among which the glass-to-metal and ring seals are the more important. The apparatus consists of five basic parts:

1. Vacuum jacket and vapor condenser.
2. Vapor lift pump.
3. Boiler.
4. Menzies-Wright differential thermometer.
5. The power supply.

The arrangement of the first four basic parts is shown in Fig. 170. The boiler, pump and thermometer are enclosed in a vacuum jacket to minimize outside temperature effects.

1. Vacuum Jacket and Vapor Condenser

The dimensions of the jacket and condenser are given in the assembly drawing, Fig. 170. These parts are fabricated and assembled as follows:

The inner jacket is made by sealing a 22-mm. tube to a 38-mm. tube. The smaller tube is cut 9 cm. from the seal. The larger tube is cut 20 cm. from the seal. This end is spun out into a flare which fits snugly into a 51 mm. tube.

2. Vapor Lift Pump

The pump consists of a boiler bell, liquid and vapor delivery tube and a liquid and vapor distributing head. A 13-mm. tube is sealed to a tube with an inside diameter of 2 mm. The large tube is cut 5 cm. from the seal and the opening is flared 45°. The liquid and vapor distributing head is made by gathering glass in the small tube at the section 11.5 to 12.5 cm. from the seal. The glass is blown out to a bulb with a diameter of 15 mm. and immediately drawn to form a bell-shaped head. The small tube is then bent to form an offset just above the seal to the large tube. The tubing adjacent the deformed bulb is then bent in a U-shape, the bend radius being about 5 mm. The excess glass beyond the maximum diameter of the deformed bulb is then cut with an abrasive wheel. If this head is properly made it will have a bell-shape and a diameter, across the bell opening, of 10 mm. Three 2-mm. beads are then formed on the edge of the bell orifice by fusing a small glass rod to the edge and cutting the rod with the burner flame. This glass is then fused until it forms a bead.

Two thin glass braces are fused to the pump in the position shown in Fig. 170. These braces should be long enough so that the pump can be centered in the inner jacket tube. After the proper lengths of the braces have been obtained by either pulling the partly-fused glass or cutting it with

the burner flame, the pump is mounted in the inner jacket assembly and the braces are sealed to the glass wall.

3. Boiler

The boiler is made by first spinning a flare on 10-mm. tubing. This flare should fit over the end of the 22-mm. tubing of the inner jacket. The flared tube is then mounted at the flared end and the tube is closed by rounding the end 2 cm. from the flare. This closed end is then dipped into 50-mesh ground glass while it is hot and the ground glass adhering to the boiler is partly fused. The surface of the boiler is completely coated by repeating the dipping and fusing operation. The coated boiler is then sealed to the 22-mm. tubing of the inner jacket.

4. The inner jacket assembly is centered in the outer jacket with glass tape as illustrated in Fig. 171. The con-



Fig. 171

denser is made as illustrated in Fig. 170. The inner jacket is then ring-sealed to the outer jacket and the condenser is sealed to the apparatus. The seal is then annealed.

5. The outside jacket is drawn down and a 19-mm. tube is sealed to the reduced end.

6. The heating element assembly is made by sealing two press welds into the glass. This is accomplished by beading the cleaned tungsten sections of the press weld with GT-70 glass. (Techniques of beading and making the press seal have previously been given.) The press flare consists of a flare of Pyrex glass 774, a graded seal between this glass and the glass 772 of the press is made of uranium glass 3320. The nickel extension lines are welded to a spiral made from a 4' length of 0.017" diameter tungsten wire. The 19-mm. tube which is the extension of the outer jacket is then cut so that the heating element when placed into the jacket will be located in the boiler. The flare and jacket are sealed and a tubulation is sealed to the flare.

7. The jacket is evacuated and tipped off as previously described.

8. An Eby vacuum tube socket is cemented to the heater end and the two heater leads are soldered to the socket prongs. Fig. 172.

4. Thermometer

A well-constructed, finely-etched and properly-filled differential thermometer is essential for good results. It is



Fig. 172

important that the bore of the glass in the two arms be constant over the distance traversed by the meniscus, in order that the capillarity correction (zero reading) may remain constant during the experiment. The ordinary instruments purchased on the market are commonly defective in this respect. The liquid with which a thermometer is filled depends on the solvent with which it is to be used. Water, having a dp/dT of 14.3 mm./°C. at 80°C. makes an ideal filling for use with benzene or other solvent boiling within a few degrees of this temperature. When, for example, acetone is to be used as a solvent, ethyl alcohol (dp/dT , 14 mm. 1°C. at 56°C.) or benzene (dp/dT 16 mm. 1°C. at 56°C.) would be preferably as thermometer liquid.

The water-filled thermometer is made as follows:

1. A 15-cm. length of 2-mm. bore capillary is sealed to an 8-mm. thin-wall tube. The capillary is cut and blown open 12 cm. from the seal. A tube 8 mm. in diameter is sealed to the opened capillary. This tube is then constricted 3 cm. from the capillary-tube seal and a 6-mm. tube cm. long is sealed beyond the constriction to serve as the filling tube and eventually as the handle of the thermometer.

2. The capillary adjacent the 8-mm thin-wall tubing is heated and a U bend is made as shown in Fig. 170. This bend is made so that the unaltered bore of the 8-mm. tube, adjacent the seal, is even with the unaltered bore of the capillary. The 8-mm. thin-wall tube is then closed so that 15 mm. of the original bore of this tube can be used for etching.

3. The thermometer is sealed to a water reservoir and the assembly is sealed to the manifold of a vacuum system, Fig. 173. The water level should be as indicated so that freezing will not break the bulb.

4. The vacuum pump is started and the system is pumped to 20 mm. pressure. The water is gently boiled by warming the bulb with a small flame. After the water is degassed by this process it is frozen with liquid nitrogen. The system is then pumped to a pressure of 10^{-5} mm. of mercury and the glass of the entire thermometer is carefully torched to remove gases. After the thermometer is outgassed and a pressure of 10^{-5} mm. is again obtained, the tubulation at A is tipped off. The ice is then melted and the water is allowed to flow into the thermometer bulb. This bulb and the capillary to C, Fig. 173, should be filled with water. The water storage bulb is then cooled and when the meniscus has retarded to D, Fig. 173 the constriction at B is quickly closed by fusing the glass around the circumference of this constriction. The water reservoir is removed and the 8-mm. tubing is closed. A glass eyelet is sealed at the closed end.

5. The thermometer is then ready to be etched. This operation can best be performed by companies which have

accurate etching facilities. (Corning Glass Works, Corning, N. Y., have such facilities.) The zero mark on both the bulb and capillary should start at the lowest part of the bulb and capillary which have the true bore of the original tubes. Fifteen 1-mm. marks are made on the bulb. The capillary is etched up to 10 cm. in mm. divisions. The centimeter divisions on both scales are numbered.

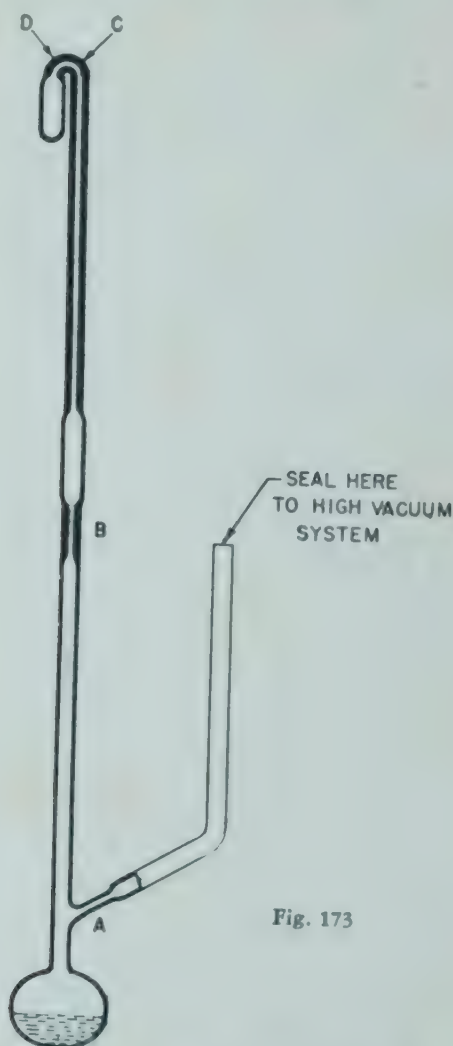


Fig. 173

The technique for filling thermometers with benzene or ethyl alcohol is different from that described for filling thermometers with water. The thermometer cannot be sealed as the meniscus is retarding in the capillary and carbonization will occur in the restriction while the glass is fused. It is necessary to cool both the reservoir and thermometer bulb and consequently the 6-mm. tubing be-

tween the restriction and reservoir must be bent in a U-shape so that both bulb and reservoir can be cooled simultaneously. The liquid and glass in the thermometer are degassed as described above. The thermometer is evacuated and the reservoir and thermometer assembly are tipped-off and the liquid is melted and allowed to flow into the thermometer bulb until the meniscus is at mark *D*. The bulb and reservoir are then cooled and the liquid in each is frozen without distilling any liquid to or from the capillary. The thermometer is then closed as before by fusing the glass at the restriction. The U-shaped tube is then cut from the thermometer and a straight section is sealed in place and the handle is made as before.

5. Power Supply

The power supply recommended is a Thordarson transformer, T-19F-99 (110-v. primary; 6.3-v. 10-amp. secondary). This instrument is put in series with a fixed resistor of 0.25 ohms (four I.R.C. "Type AB" 10-w. 1-ohm resistors in parallel) and a variable resistor (Ohmite "Type J" power rheostat, 0.5 ohms, 10 amp.). The circuit is fused for 10 amperes (secondary). Since the heating coil cannot be duplicated absolutely from instrument to instrument, the fixed resistor may have to be changed slightly. In general, it is believed that the suggested circuit is sufficiently flexible so that good boiling can be obtained in any apparatus simply by adjusting manually the power rheostat. The instrument operates at 8 to 9 amperes, with a power consumption of 25 to 30 watts.

WORKING RANGE OF THE APPARATUS

Any apparatus which makes use of the ebullioscopic method is subject to limitations in molecular weights which it will handle. The lower limit is governed by the rule that the solute being investigated must have a negligible vapor pressure at the boiling point of the solvent. For the most common solvent, benzene, the lower limit may be perhaps 160 to 170, if the material is pure. In the case of a material like a petroleum oil, which contains a large number of compounds, the most volatile components present must be considered; as a result, it may be impossible to run materials of average molecular weight less than 200 to 250.

The upper limit in molecular weight is variable. Materials having as high a value as 1000-2000 have been run successfully; in special cases products of even higher average molecular weight have been analyzed with apparent success.

SELECTION AND PURIFICATION OF THE SOLVENT

The first point to be considered is the selection of an appropriate solvent. Theoretically, almost any organic

liquid* having a satisfactory ebullioscopic constant could be used. From a practical standpoint, the number of substances which can be employed is relatively small. This is a consequence of two requirements which the solvent must meet.

In the group benzene, cyclohexane and carbon tetrachloride, benzene is outstanding. Not only is it a versatile solvent, stable, and chemically inert, but it can be prepared in a high and consistently reproducible state of purity. For this reason, work in a laboratory has been done almost exclusively with this solvent. The particular advantage gained in the matter of purification will be evident in the following discussion.

Benzene in the "CXP" or, even better, in the "reagent" grade is one of the purest chemicals available today. Ebulliometric experiments have shown that it is impossible to purify such benzene further by any process of rectification. Improvement can be gained by cryoscopic means. Thus, by recrystallization, "CXP" benzene (F.P.— $5.40^{\circ}\text{C}.$) can be raised to "reagent" grade (F.P.— $5.50^{\circ}\text{C}.$). "Nitration" grade (F.P.— $5.20^{\circ}\text{C}.$) is hardly to be recommended for molecular weight work. It is absolutely essential to remove the water, however, but, since the benzene-water azeotrope boils at $68^{\circ}\text{C}.$, as against $80^{\circ}\text{C}.$ for the pure benzene, only simple distillation is necessary to prepare it for use; a particular technique is required to be sure that this water removal is complete.

In the past, only imperfectly-dried benzene had been employed. Despite this, precisions of one percent or better were obtained, since the solvent was calibrated for the conditions under which it was being used. Complete removal of the

*Water is unsatisfactory. The instrument was designed primarily for organic solvents. The latent heat of water is so high that, even at maximum power input, the boiler cannot be maintained full of vapor.

(1) *Boiling Temperature.*—Obviously, a highly volatile or involatile solvent would not be suitable. The boiling range is even more restricted, however, because of the thermometer filling. As pointed out above, the water thermometer has the best sensitivity (dp/dT) at about $86^{\circ}\text{C}.$ Above this point it increases, eventually becoming too sensitive for good operation; below it the temperature response is less and, ultimately, becomes too small to be practical.

Thus, benzene, cyclohexane, carbon tetrachloride, methyl ethyl ketone, isopropyl alcohol, etc., are satisfactory with respect to boiling temperature. Other solvents boiling at lower or higher temperatures are less desirable.

(2) *Purity of Solvent.* To show the necessary low, steady zero point on the thermometer, a solvent must be pure. It is almost impossible to set a limit for allowable impurities, since this would depend in part on the accuracy desired in the results. It will suffice to say that, of the several solvents listed above, only benzene, cyclohexane, and carbon tetrachloride can be purified with ease.

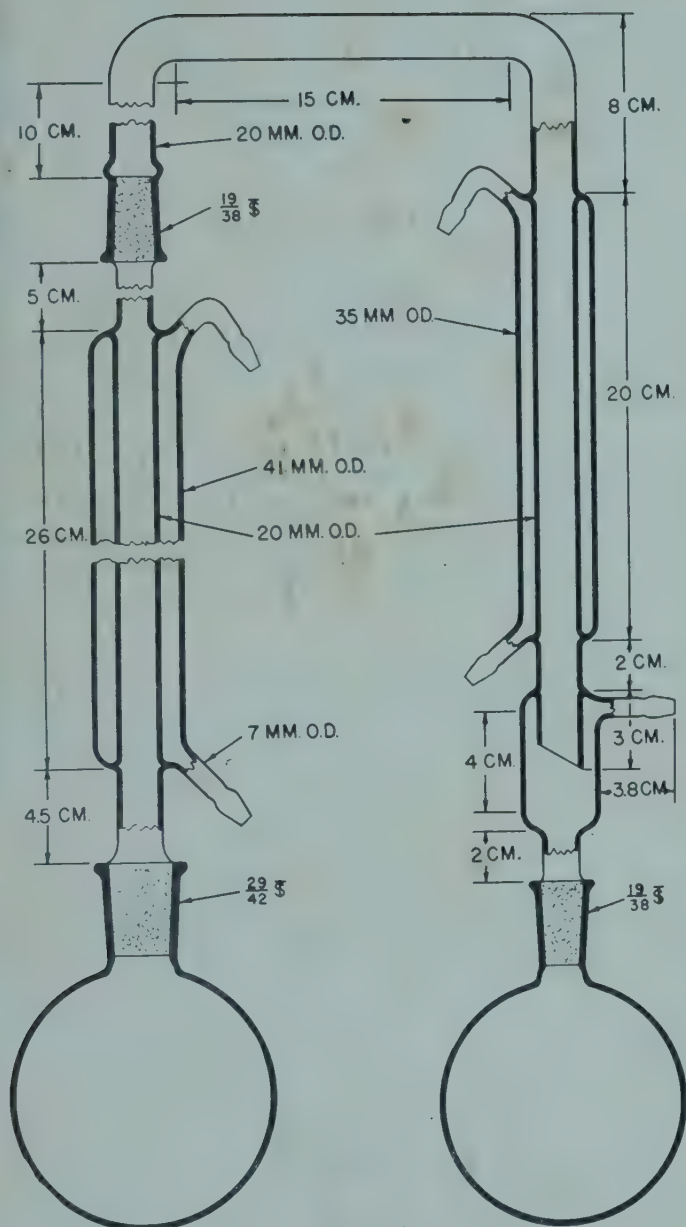


Fig. 174

water, however, has eliminated the most important of the remaining causes for irregularity and has resulted not only in an improvement of the precision by at least 0.5% but has made for a much smoother and more rapid determination.

A three-liter round-bottom flask is set up with a vertical water condenser attached to the flask through a ground glass joint, Fig. 174. (No grease!) The upper end of the condenser tube is bent through two right angles into an inverted U and connected through a ground glass joint to a second condenser parallel to the first. A receiver with a vent is attached to this second condenser through an appropriate joint.

Benzene is charged to the flask and heated to boiling; a Glas-Col heating mantle is recommended. Water is circulated through the two condensers. The water precipitating from the condensing azeotrope will be seen shortly as a milky band in the first condenser. When the water is thus sharply defined in this tube, the cooling water is withdrawn, allowing the condenser to become warm. The azeotrope now progresses slowly over to the second condenser where it again can be seen as it passes on into the receiver. To clear this second condenser, the coolant is withdrawn and hot vapor allowed to pass through it briefly. A drying tube (CaSO_4 anhyd.) is attached quickly to the receiver vent and water turned into the second and then into the first condenser. If the water removal has not been complete, the line of condensation in the first condenser will still show signs of cloudiness.

When properly handled, this method allows for complete and controlled removal of the water in a sample of benzene. It should be noted that the same process cannot be carried out in an ordinary rectifying still, except under special conditions. This is a consequence of the manner in which the still heads are commonly constructed.

As soon as it has been determined that water removal is complete, the condensers are removed and replaced by a stopper (no grease!) having a tube through it which reaches to the bottom of the flask. The tube extends over in the form of an inverted U ending in a stopcock (no grease!) with a burette tip. By forcing dry air (CaSO_4 anhyd.) into the flask through a side tube in the stopper, dry benzene can be delivered when needed to the Bailey weighing burette as described below.

CALIBRATION OF THE THERMOMETER

The clean and dry instrument is set up. In this calibration, as in every subsequent run, cleanliness is essential. The apparatus is washed with the same solvent which is being used in the molecular weight determinations (not the calibrated material, however) and the apparatus dried in a current of dry air until no remaining benzene is visible on the heating cone, in the pump, or at the ring seal at the base of the condenser. Experience has shown that the solvent clings to these places longest. If rinsing the equipment is not sufficient, boiling some of the solvent in the apparatus

will remove any soluble material. In extreme cases, chromic acid or other cleaning agent may be used. Should water be present in the boiler, it is better that benzene be added and allowed to boil over the top of the condenser than to attempt to remove it by the use of some other solvent. The thermometer also should receive attention to be sure that no solute or other material adheres to it, particularly between the supporting ring and the glass stem.

A Bailey burette is filled with the purified benzene by injecting dry air into the three-liter storage flask as explained in the previous section. The benzene remaining in the stopcock and the tip of the tube should be discarded before withdrawing new solvent. About 25 grams (about 28 cc.) of the benzene is transferred to the apparatus; no weight is required for this thermometer calibration experiment.

The thermometer is now set in place, taking care that the vanes of the brass or bronze supporting ring are so adjusted that the instrument hangs vertically. Sufficient tension should be exerted by the vanes to hold the lower thermometer bulb firmly against the inverted cup of the pump. Failure to observe the latter precaution will invariably result in unsteady readings. A drying tube (CaSO_4 anhyd.) is placed in the top of the condenser and the coolant water turned on. It will be well to observe this sequence with respect to the condenser water to avoid exposing a cold inner surface to moist air during the addition of the benzene.

The temperature of the condenser water should be kept at 20°C . or below to assure a negligible loss of solvent. During warm days, it may be necessary to precool the tap water with ice; care should be taken, however, not to drop the temperature below the freezing point of the solvent. Under proper operating conditions, condensation is complete on the supporting ring and at the base of the condenser.

Heat is applied and the solvent allowed to boil for about a half hour. The rheostat is adjusted to a point where an intimate mixture of vapor and liquid is thrown over the bulb, and the vapor condensation line has reached the base of the condenser. Unless the instrument is filled with vapor, water remains in the upper bulb of the thermometer. The extremes in boiling, in which large slugs of solution or a stream of vapor is forced through the pump, are to be avoided. Actually, there will be a range in heat-input over which no change in thermometer reading as observed. Experience has shown that, even when a solute is present, the setting can be changed somewhat without altering the reading although, at higher rates of boiling more solvent is on the walls of the apparatus and, hence, the concentration and the boiling point are higher. Readings are now taken

on the long and short arms of the thermometer; their difference is the zero value, or that proportion of the height of water which can be attributed to capillary effects. Strong light on either of the thermometer bulbs is to be avoided, except for the few moments required to take a reading.

Establishing the correct zero point is one of the most important operations. The value depends on four factors:

1. The boiling temperature.
2. Thermometer dimensions.
3. The liquid used for filling thermometer.
4. The purity of the solvent.

Since, for any given thermometer and solvent type, the first three factors are constant, the fourth item is the only one to be considered. If the thermometer were immersed in a thermostat at, say, 80°C ., both bulbs would be at precisely the same temperature and the difference in level would be wholly dependent on the difference in the dimensions of the two arms. In the instrument, however, the upper bulb is at the condensing temperature of the solvent and, unless the material is absolutely pure, it will be slightly cooler than the lower bulb (boiling temperature). Thus, the zero correction is slightly greater than that due to capillarity.

This zero reading is the first check on the cleanliness of the apparatus and the purity of the solvent. Ebulliometric studies have shown that the difference in the boiling and condensation points for dehydrated "reagent" benzene is 0.008°C . and does not vary over 0.001°C . from this value. "Reagent" benzene, after removal of water in the manner described, will always give exactly the same zero reading for any given instrument and thermometer. If it varies by more than say 0.02 cm. (0.001°C .) on the water scale, contamination can be presumed. "CXP" benzene exhibits a boiling-condensation temperature difference of 0.010°C . to 0.015°C . depending on how much benzene is removed in azeotroping the water. If the procedure is carried out in about the same manner each time, duplicate batches of "CXP" benzene will have exactly the same zero, if the stock supply is the same. A new stock will yield purified material having a consistent zero but differing somewhat from the first. Our practice is to set aside five or ten gallons of stock benzene (CXP) and prepare two or three liter batches from this supply.

The advantage of this constant zero point will be seen in the calibration of the solvent. For any given instrument and thermometer, it has been shown that a new batch of benzene having the same zero as the old batch will have exactly the same ebullioscopic constant and, hence, need not be further calibrated.

For convenience in later runs it is important that the relationship between the readings obtained on the long arm

and those on the short arm be determined. To do this a small amount of an involatile solute is added, enough to cause a rise of a few millimeters of water on the thermometer. Readings are now taken on both arms, according to the prescribed method. More solute is now added and the process continued, taking several readings over the entire thermometer scale. When the long-arm values are plotted against the short-arm values, the graph obtained should, for a well-constructed instrument, be perfectly linear. It is possible that slight curvature may be noted as one nears the zero point. As an aid in later calculations it will be found convenient to plot the long-arm reading against the net rise, the latter being calculated as the difference in the levels in the two arms minus the zero reading for the instrument. Thus, during any determination, a single reading on the long arm is sufficient to fix the net height of the water column. It may be mentioned that a value of Δh obtained from the graph is much more reliable than that obtained by the use of any single reading on the short arm, since short arm readings are, in general, difficult to get exactly.

CALIBRATION OF THE SOLVENT

Calibration of the solvent to be used is essential as the commonly published ebullioscopic constants are not applicable. The chief reason for this is that the actual amount of the solvent in the liquid phase, and hence the absolute concentration, is not known. Since very nearly the same amount of benzene is used each time, since the boiling rate is the same, and since the vapor condenses totally at the base of the condenser, a constant fraction of the solvent is removed from the liquid phase and this factor enters into the K which one determines by running a compound of known molecular weight.

Any compound which may be purified easily and which possesses a reasonable solubility in the solvent being used will serve as a calibrating compound. In general it is believed that compounds should be used which are of similar chemical type to those which are to be examined later. Particularly to be avoided are those compounds which are polar in nature, as these materials frequently exhibit a molecular weight-concentration slope. The necessary extrapolation of the apparent K value to zero concentration is a possible source of error and hence is to be avoided. Experience in this laboratory has shown that triphenyl methane, meta-diphenyl benzene, anthracene, and benzil are especially satisfactory as standards. Regardless of the purification process used for any particular compound, it is advised that the final step be a recrystallization from the solvent to be employed in the molecular weight determinations, followed by a drying of the powdered material in high vacuum. The retention by the crystals of a volatile sub-

stance other than the solvent being used in the molecular weight determination may introduce a large error. Before use, it is convenient to form the purified crystals into pellets, each of about 0.2 g. Materials so purified can be kept almost indefinitely.

Into the clean and dry instrument there is now weighed by means of the Bailey burette about 25 grams (28 cc.) of the purified solvent, care being taken in the withdrawal and transfer as previously described. The Bailey burette is particularly recommended for cutting evaporation losses and avoiding exposure of the solvent to moist air. The thermometer is inserted, the drying tube (CaSO_4 anhyd.) placed at the top of the condenser, and the coolant water turned on.

Heating is now begun and the solvent allowed to boil for about twenty minutes. By this time the apparatus has been brought to temperature and the thermometer should have attained a steady reading. The zero point may now be checked. While the apparatus is coming to temperature, about a gram of the purified solute is placed on a watch glass and weighed to the nearest 0.1 mg. At the end of the 20-min. period, or as soon as the zero point has been checked, the drying tube is taken from the top of the condenser and small pellets of the solute added, taking care that none strikes the condenser wall or lodges in the ring supporting the thermometer. This process becomes easy after a little practice. As soon as the addition has been made, the drying tube is replaced and the watch glass containing the solute weighed again in preparation for the next addition. Under normal conditions, the solute dissolves almost immediately and a reliable temperature reading can be made at the end of five minutes. Occasionally, during an actual molecular weight determination, additions of several tenths of a gram of solute is necessary (high molecular weight compounds). The thermal disturbance resulting from the addition of such an amount of cold solute may be so great that more than five minutes will be required for the apparatus to come to equilibrium. A steady thermometer reading is, of course, the criterion. A second portion of solute is now added and the process repeated until in all four or five additions have been made. At some time during the run the pressure (corrected to $0^\circ\text{C}.$) should be taken; unless the run is unduly prolonged, this one reading will suffice for the determination. In general the run should not last over one and a half to two hours, not only for reasons of changing pressure but also for the sake of convenience. Loss of solvent under these circumstances is, of course, less.

For liquids, a small vial equipped with an eye-dropper is filled with the material and weighed. Adding the liquid through the condenser by means of the eye-dropper presents no greater difficulty than the addition of the solid pellets as previously described. Vial, eye-dropper, and liquid are weighed again after the addition. For liquids which are sufficiently involatile to be run in this apparatus, no evaporation losses are observed. In cleaning the eye-dropper, care must be taken that the solvent used for cleaning is not absorbed by the rubber bulb. This has been observed to happen particularly when benzene is employed, with the result that the eye-dropper slowly loses weight over a period of time as the solvent evaporates.

The usual formula for calculating the ebullioscopic constant applies.

$$K_b = \frac{\text{Mol. wt. of solute} \times \text{wt. solvent} \times \Delta t}{\text{Wt. of solute} \times 100} \quad (38)$$

Here Δt is the rise in the boiling point in centigrade degrees and K_b the constant in centigrade degrees rise in boiling point per mole of dissolved solute per 100 g. solvent.

Tables are given by Menzies³ for converting the reading obtained on the water thermometer (cm. H₂O) to centigrade degrees, but the process is too laborious to be used in routine work. The following procedure is to be preferred.

Calculate values for the constant for each addition of solute in each run using, instead of Δt in centigrade degrees, the value in centimeters of water; this will be the long-arm reading on the thermometer minus the short-arm value (obtained from the prepared chart), minus the zero point. A series of figures, referred to as K_{H_2O} values, will be obtained. These values are a function of the barometric pressure and the temperature. Assuming benzene to boil at 80.110°C.⁴, the following table of factors has been prepared for converting K_{H_2O} values to the pressure- and temperature-independent absolute constants (K_b).

	mm. Hg Pressure			
Δt (cm. H ₂ O)	750	740	730	720
0	1.991	1.962	1.933	1.904
5.0	2.009	1.979	1.950	1.921
10.0	2.026	1.996	1.968	1.939

The constants so obtained may be averaged and the mean deviation should not exceed $\pm 0.5\%$.

Once the value of the absolute constant has been determined, a table can be constructed, again by use of the factors, giving K_{H_2O} as a function of pressure and Δt . For illustration two typical calibration runs are cited together with the necessary calculations.

Instrument #2 Solute: m-Terphenyl, M.W. 230.29
 Thermometer A Benzene (batch #2) 26.377 gms.
 Thermometer zero 0.73 ± 0.01 cm. H_2O $P = 731$ mm. (corr.)
 Cumulative wt.

Solute, gms.	Δt cm. H_2O	K_{H_2O}
0.3330	$4.44 - 0.79 - 0.73 = 2.92$	53.40
0.4381	$5.27 - 0.67 - 0.73 = 3.87$	53.65
0.5357	$6.02 - 0.57 - 0.73 = 4.72$	53.50
0.5993	$6.50 - 0.50 - 0.73 = 5.27$	53.40
0.6822	$7.15 - 0.41 - 0.73 = 6.01$	53.50
0.7517	$7.67 - 0.33 - 0.73 = 6.61$	53.40

Using appropriate factors,

$53.40/1.946 = 27.45$	$53.50/1.952 = 27.40$
$53.65/1.949 = 27.52$	$53.40/1.954 = 27.34$
$53.50/1.957 = 27.34$	$53.40/1.959 = 27.28$
Av. $K_b = 27.39 \pm 0.07$	

It will be observed that we are working on the border line of our limits in precision. Thus, it would have done just as well in this case to have averaged the K_{H_2O} values and divided by an average value for the conversion factor ($\Delta t = 5.0$), thereby neglecting the dependence of the factor on Δt . In some cases, however, such as the last illustration in the next section, where a fair range in Δt is covered and, particularly, where there is a molecular weight-concentration slope, the error is not negligible.

Having found the average K_b value to be 27.39 ± 0.07 we can construct a chart for use in subsequent molecular weight determinations from which the proper value for K_{H_2O} for this instrument, thermometer, and solvent can be picked off, knowing the pressure and Δt . Thus for $P = 740$ mm.

Δt cm.	K_{H_2O} (740)
0.0	$27.39 \times 1.962 = 53.74$
0.5	$27.39 \times 1.979 = 54.21$
1.0	$27.39 \times 1.996 = 54.62$

The process is repeated for other pressures and isobars drawn on Δt , K_{H_2O} coördinates at intervals of one millimeter. The plots are linear and calculation for each 10 mm. and dividing off the intervening space into ten parts is sufficient.

To illustrate the fact that a second batch of benzene from the same stock will have the same ebullioscopic constant if the zero point is the same, the following is quoted.

Instrument #2	Solute: m-Terphenyl, M.W. 230.29			
Thermometer A	Benzene (batch #3) 26.912 gms.			
Thermometer zero 0.72 ± 0.01	$P = 725$ mm. (corr.)			
Cumulative Wt.	Δt	Calc'd.		
Solute, gms.	cm. H_2O	K_{H_2O}	Factor	K_b
0.4785	4.06	52.60	1.933	27.21
0.5521	4.70	52.77	1.935	27.27
0.6185	5.27	52.78	1.937	27.29
Av. $K_b = 27.26 \pm 0.03$				

Therefore, if succeeding batches of benzene, with the same instrument and thermometer, show the same zero

point, the same ebullioscopic constant may be used. If a different zero is observed, which cannot be brought to the old value by further removal of water or cleaning the apparatus, a new calibration must be run. A check run with a compound of known molecular weight is occasionally made for checking one's own technique, even though the zero point of the solvent has not changed appreciably.

DETERMINATION OF A MOLECULAR WEIGHT

For determining a molecular weight on an unknown substance, exactly the same procedure is used as for the solvent calibration runs, except that the unknown is added instead of the calibration compound. A few typical runs are cited here to show, in one case, the accuracy and, in others, the precision which is possible to attain. The oils are highly refined, stable paraffinic petroleum products which were selected for molecular weight standards.

Instrument #2	Solute: Triphenyl Methane		
Thermometer A	Benzene (<i>batch #2</i>) 26.147 gms.		
Thermometer Zero 0.70 ± 0.01	$P = 726$ mm. (corr.)		
Cumulative Wt.	Δt		
Solute, gms.	cm. H ₂ O	K_{H_2O}	Mol. Wt.
0.3609	2.98	52.88	245.0
0.4294	3.57	52.94	243.5
0.5090	4.24	53.01	243.4
0.6199	5.15	53.09	244.3
0.7235	5.99	53.17	245.3
Av. Mol. Wt. = 244.3 ± 0.7			

Thus, using the benzene calibrated against purified *m*-terphenyl, a value for triphenyl methane is obtained which compares favorably with the theoretical value of 244.32.

A run was made on Molecular Weight Standard GA.

Instrument #1	Solute: Molecular Weight Standard GA.		
Thermometer #3	Benzene (<i>batch #1</i>) 26.830 gms.		
Thermometer zero 1.38 ± 0.02	$P = 746$ mm. (corr.)		
Cumulative Wt.	Δt		
Solute, gms.	cm. H ₂ O	K_{H_2O}	Mol. Wt.
0.4449	2.99	53.92	299.0
0.6200	4.19	54.22	298.5
0.7900	5.36	54.35	299.0
Av. Mol. Wt. = 299.0 ± 0.2			

Repeating this oil with a different instrument, different thermometer and different benzene, we get the following:

Instrument #2	Solute: Molecular Weight Standard GA		
Thermometer A	Benzene (<i>batch #2</i>) 26.206 gms.		
Thermometer zero 0.73 ± 0.02	$P = 731$ mm. (corr.)		
Cumulative Wt.	Δt		
Solute, gms.	cm. H ₂ O	K_{H_2O}	Mol. Wt.
0.5324	3.67	53.35	295.5
0.7940	5.47	53.52	299.0
1.0466	7.15	53.67	296.5
1.2782	8.70	53.80	301.5
Av. Mol. Wt. = 298.0 ± 2.0			

The following are two check runs on Molecular Weight Standard CB using different batches of benzene.

Instrument #2 Solute: Molecular Weight Standard CB
Thermometer A Benzene (batch #1) 26.309 gms.
Thermometer zero 0.82 ± 0.02 $P = 736$ mm. (corr.)

Cumulative Wt. Solute, gms.	Δt cm. H ₂ O	K _{H₂O}	Mol. Wt.
1.1064	3.63	54.18	630
1.3092	4.30	54.25	628
1.7393	5.67	54.37	633
1.9623	6.50	54.46	624
Av. Mol. Wt. = 629 ± 2			

Instrument #2 Solute: Molecular Weight Standard CB
Thermometer A Benzene (batch #2) 25.412 gms.
Thermometer zero 0.71 ± 0.02 $P = 732$ mm. (corr.)

Cumulative Wt. Solute, gms.	Δt cm. H ₂ O	K _{H₂O}	Mol. Wt.
0.8644	2.88	53.36	630.5
1.2031	4.03	53.47	627.0
1.4804	4.97	53.55	627.5
1.7399	5.89	53.63	625.5
Av. Mol. Wt. = 627.6 ± 1.4			

In the large majority of cases, the several values for the molecular weight obtained in a single determination may be averaged arithmetically as was done in the above illustrations. Occasionally, however, it is observed that the molecular weight value does change with concentration and the slope of the molecular weight-concentration curve may be positive or negative. The positive case is rare; it is observed for polar compounds such as acids and even a few light oils. Presumably, the effect is one of association in solution. Among high-molecular-weight materials, a negative slope is frequently encountered. The explanation is unknown but the effect is well established. Certainly in such large mass concentrations as are necessary for these materials to get the desired temperature rise, the solution is far from ideal and it is hardly to be expected that the simple law could be used for calculating the molecular weight without error.

In either case, an attempt is made to obtain the correct value for the molecular weight by extrapolation to zero concentration of solute. For want of a better method, the best straight line is drawn and the error involved will depend on how closely the data conform to the linear relationship. Agreement among check determinations may be within one percent, although one cannot claim that this will be true under all circumstances. The following are check runs on our Molecular Weight Standard R which exhibits a definite negative molecular weight-concentration slope.

Instrument #2 Solute: Molecular Weight Standard R
Thermometer A Benzene (batch #2) 24.206 gms.
Thermometer zero 0.73 ± 0.02 $P = 734$ mm. (corr.)

Cumulative Wt. Solute, gms.	Δt cm. H ₂ O	K_{H_2O}	Mol. Wt.
2.7490	3.58	53.60	1513
3.0280	4.01	53.63	1487
3.4660	4.70	53.69	1454
3.8665	5.36	53.76	1425
4.3026	6.07	53.81	1402
4.7434	6.87	53.88	1368

$$\text{Extrap. Mol. Wt.} = 1637 \pm 10$$

Using a different batch of benzene a check run was made.

Instrument #2	Solute: Molecular Weight Standard R		
Thermometer A	Benzene (<i>batch #3</i>) 27.340 gms.		
Thermometer zero	0.73 \pm 0.02	$P = 736$ mm. (corr.)	
Cumulative Wt.	Δt		
Solute, gms.	cm. H ₂ O	K_{H_2O}	Mol. Wt.
3.079	4.08	53.96	1488
3.366	4.55	54.00	1460
3.797	5.20	54.05	1440
4.240	5.96	54.12	1407
4.610	6.61	54.17	1383

$$\text{Extrap. Mol. Wt.} = 1640 \pm 10$$

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2. A. W. C. Menzies and S. L. Wright, *Journal of the American Chemical Society*, Vol. 43, (1921), Page 2314.
3. A. W. C. Menzies, *Journal of the American Chemical Society*, Vol. 43, (1921), Page 2312.
4. W. Swietoslawski, Ebulliometric measurements, Reinhold Publishing Corp., 1945.

CHAPTER XIV

SWIETOSLAWSKI EBULLIOMETERS

A. DESIGN

[This chapter was written in collaboration with Dr. John R. Anderson, Mellon Institute of Industrial Research*]

Any kind of apparatus designed for carrying out determinations of the boiling points of liquid substances or solutions may be called an ebulliometer. This term, however, is usually associated with the precision devices invented by the Polish scientist, W. Swietoslawski.¹ By using this equipment, in conjunction with adequate thermometric instruments, the boiling temperature of liquids and solutions, and the condensation temperature of vapors, may be measured with a precision of $\pm 0.001^\circ\text{C}$.

Precise ebulliometric measurements require not only specialized apparatus, the construction of which is presented here, but also specialized techniques based on the principle of comparative measurements; the techniques have been described in an authoritative monograph¹ which should be perused by all investigators prior to application of the ebulliometric method.

In addition to their use for precise determinations of boiling points and condensation temperatures, ebulliometers may be employed for determination of the ebulliometric degree-of-purity of liquid substances and azeotropes; calibration of thermometers; measurement of changes in pressure; determination of the impurity content and moisture content of liquid and solid substances; study of azeotropy; determination of the amount of vapors adsorbed by solid substances; examination of thermal resistivity of liquids and solids; molecular weight determinations; examination of physico-chemical standards, and the determination of solubility and equilibrium constants.

Standard Ebulliometric Elements

In 1942 J. R. Anderson, in consultation with Professor Swietoslawski, undertook the design of a set of standard ebulliometric elements provided with standard ground joints, from which almost any kind of ebulliometer might be arranged. These standard elements, shown in Fig. 175, were constructed by one of the authors of this book. Their use has simplified the construction of ebulliometers to the extent that they are now replacing the previous designs. For

*Acknowledgement is gratefully made to Professor W. Swietoslawski for suggestions made during the writing of this section.

¹W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, 1945.

this reason most of this chapter is devoted to a description of them.

Element A (Fig. 175) constitutes the boiling-temperature section of all ebulliometers in which boiling temperatures are to be measured. It consists essentially of a spherical reservoir (which is partly filled with the liquid under examination), a cylindrical activated boiler, a thermometer well, and a drop counter. The theory of its functioning has been elaborated on elsewhere.¹ B. is a condensation temperature element which may be used in all ebulliometers in which one or more condensation temperatures are to be measured. C is a rectifying column without packing, for use in differential or multistage ebulliometers in which only moderate rectification of vapors is desired. Element C may also be used, like element D, as an ordinary condenser. Elements D and E form, together, a special condenser system so designed that moisture may be removed from the substance under examination by distillation of a very small amount of material. E is also equipped with a ground joint for holding element H (a receiver for collection of small amounts of distillates containing moisture), and with a side-arm for connecting the assembled ebulliometer to a "manifold" (to which other ebulliometers each operated under the same inert atmosphere and under the same pressure, may be adjoined). It is sometimes convenient to seal the side-arm of element E to the manifold through a 3-way stopcock of large bore; in this way one may isolate any one ebulliometer from the others. Alternatively, the side-arm may be connected directly to a drying-tube.

Element F is a conventionally-packed fractionating column with a side-arm sealed, just below the heated section, to the central tube. Element G is an ordinary round-bottomed flask, and I is an inner ground joint to which has been sealed an ordinary stopcock. The usefulness of the latter element will be apparent later.

It has previously been emphasized that ebulliometers constructed with ground joints cannot be used for tonometric measurements.¹ In addition, it has now been found by experience that it is rather difficult to assemble firmly, from the standard elements, complicated ebulliometers—especially after the elements have been properly insulated. Difficulties also arise in removing moisture, as a heteroazeotrope, from an ebulliometer constructed with ground joints. Heteroazeotropes condense in the joints, for the latter must not be lubricated, and the water may leak back into the vapors of the substance under examination (even after several hours of operation). To heat the joints with a gas flame¹ is not always an adequate solution, particularly if the joints themselves must be well insulated.

For these reasons, it is recommended that, for very precise work, the use of ground joints other than the one for holding the receiver, shown on element E (Fig. 175), should be abandoned. Standard elements *without* ground joints should, however, be retained during construction, shipment, and assembly of the apparatus. Almost any kind of ebulliometer may be constructed by sealing the various elements together in the laboratory in which the apparatus is to be used. Ebulliometers of one kind may then be transformed into those of another simply by removing certain elements and resealing

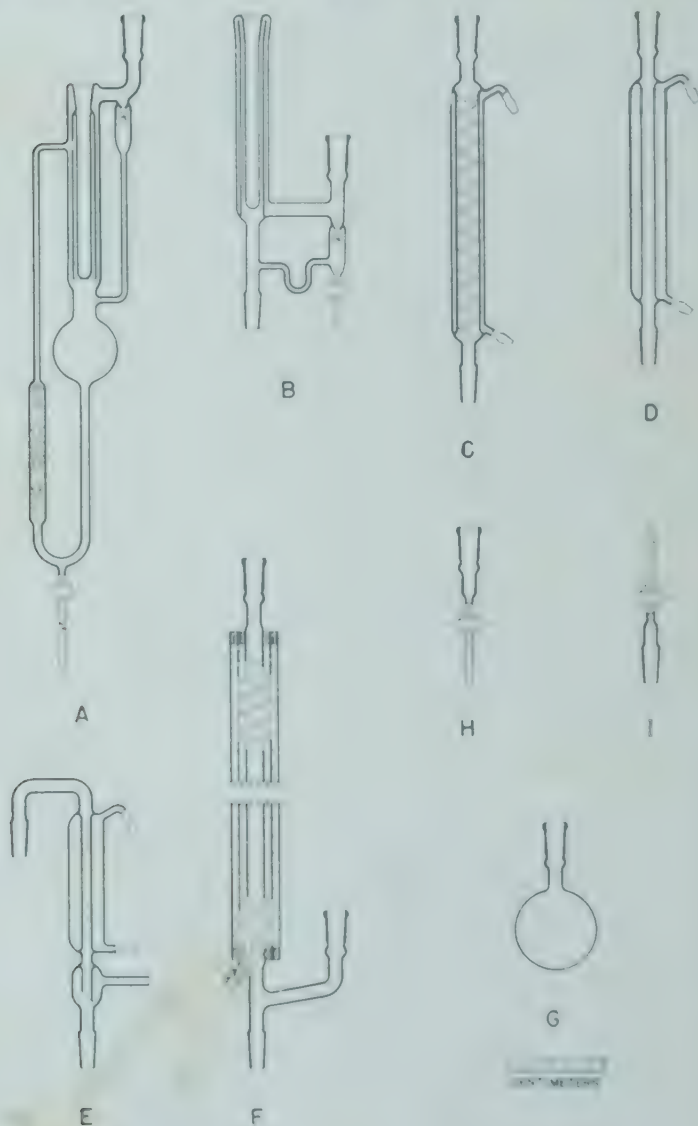


Fig. 175

them in another position. In all cases, the only seals required for this purpose are of tubing of 16 mm. diameter. It should be emphasized, however, that in some laboratories standard elements with ground joints are used successfully.

Beckman-thermometer Wells

The thermometer-wells in elements A and B (Fig. 175) have been designed to accommodate long-stemmed Beckman thermometers. The disadvantages of thermometers of this type have been enumerated¹ and, as has also been pointed out¹, if improved Beckman thermometers should become available in the future in the United States, the wells in elements A and B may then be shortened. Most of the difficulties encountered in using Beckman thermometers are associated with improper design of the tube connecting the mercury bulb with the capillary which covers the scale of the thermometer. If, however, ebulliometers are adapted to this thermometer, and if the experimenter avails himself of an appropriately-chosen method of comparative measurements, accurate results are obtainable. In the United States there has been a tendency to discard the Beckman thermometer in favor of the more costly platinum-resistance instrument. The correct solution, however, is to plan the experiment well (by basing it on the comparative principle). One may then obtain excellent results without using expensive temperature-measuring equipment.

In order that element B may function properly, vapors must first pass upwards *around* the thermometer-well and then downwards to the side-arm leading to other parts of the apparatus. If the hydrostatic pressure of the liquid in the U-tube of this element does not exceed the "vapor head" established around the thermometer-well, or if, at the start of the experiment, *total* condensation takes place around the thermometer-well, vapors may pass through the U-tube. So as to circumvent this difficulty where it arises, i.e. if high boiling liquids are being examined, the U-tube should be made somewhat deeper, especially when element B is connected directly with condenser element D as in Fig. 179. An artifice often convenient for overcoming this difficulty consists in heating the condensation element with an auxiliary heater which will be described in detail later. Of course, elongation of the U-tube of element B influences unfavorably the liquid "hold-up" of the apparatus.

Just enough mercury to cover the bulb of each Beckman thermometer is placed in the respective wells before the ebulliometers are put in action, and the mercury is then covered with a thin layer of mineral oil. It has been pointed out that it is necessary to keep the hydrostatic pressure (exerted by the mercury¹) constant in the various wells into which the thermometers are successively transferred. It has also been emphasized that the presence of mercury in the

well creates a constant danger that the experimenter might be poisoned by mercury vapors.¹ In addition, it is important to keep the thermometer reasonably well centered in the mercury in order to avoid direct contact between the bulb and the well walls.

These three problems are not unrelated, yet no adequate simultaneous solution to all of them has previously been given. The solution is actually quite simple. First, a group of well-matched thermometers should be selected. Their bulbs should be as uniform as possible as to diameter and to length. In addition, the diameter of the tube containing the

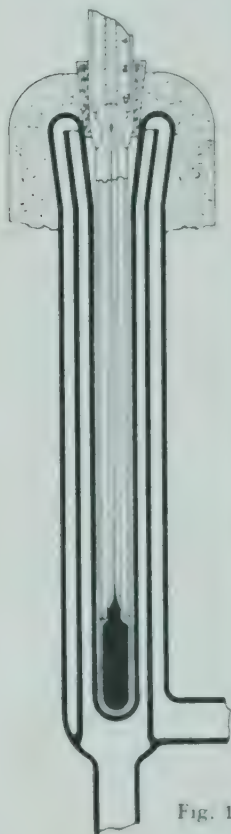


Fig. 176



Fig. 177

long "capillary" connecting the thermometer bulb and scale capillary should be the same for all thermometers chosen, and the position of the seal between this "housing" and the scale "housing" should in each thermometer be the same distance away from the bulb. These conditions are not difficult of fulfilment if the thermometers have all been manufactured by the same firm, but thermometers from different firms are likely to be far from uniform. Secondly, until standard specifications have been established for Beckman thermometers, the ebulliometers should be constructed to

suit one of the matched instruments. The height and diameter of the thermometer-wells, and their shape in their upper section, should be such that a small portion of the scale "housing" will be surrounded by the insulation which covers the thermometer-well (see Fig. 176). A tight-fitting relatively long rubber stopper should be placed around the thermometers at such a position that, with the well uninsulated, part of the stopper fits snugly in the top of the well. Insulation, to be described in detail later, is now applied at the top of the well so that it fits around the upper part of the stopper. Two pieces of relatively wide Nichrome ribbon, or other suitable conductor not corrodable by mercury, should be placed under the stopper and on opposite sides of the thermometer from about one inch above the stopper down to the top of the bulb. These ribbons, which are not shown in Fig. 176, may be held in close contact with the thermometer with cellulose tape or threads. An amount of mercury just sufficient to make contact with the lower ends of the ribbons (when the thermometer is in place) should now be put in each well. A "test for contact" consists in using the mercury in the well as a switch which will turn on a tiny light-bulb when both ribbons touch the mercury. A convenient device for completing the circuit is shown in Fig. 177. It consists of a small "dry" cell with a very small light-bulb soldered onto the positive pole, and a pair of leads, one from the other bulb terminal and one from the shell of the "dry" cell. When adjusting the position of the thermometer, the leads from this device are put into contact with the upper ends of the ribbons; the thermometer is in the correct position when vertical movement of the thermometer through about one millimeter will just make or break the electric circuit, as evidenced by the light.

Ebullimeters from Standard Elements

Elements A, D, and E (without connecting ground joints) may be combined as shown in Fig. 178 to form a simple ebullimeter. A differential ebullimeter for molecular weight determinations, constructed from elements A, B, D, and E is shown in Fig. 179. Elements A, C, B, D, and E have been arranged, as shown in Fig. 180, to form a differential ebullimeter for determination of the ebulliometric degree-of-purity of liquid substances or of homoazeotropes. Element H may be used in conjunction with these apparatuses when one desires to remove a small amount of distillate containing moisture.

If the problem of the experimenter is simply that of measuring boiling temperatures of liquids or solutions, and if he has at his disposal equipment for making, with the desired accuracy, absolute temperature and pressure measurements, a simple ebullimeter (Fig. 178) is all that is required. On the other hand, should it be desired to carry out comparative

ebulliometric measurements, two ebulliometers, one of which is differential (Fig. 179 or 180) should be employed.

For simultaneous measurements of boiling and condensation temperatures without appreciable rectification of the vapors (as in molecular-weight studies) a differential ebulliometer of the type shown in Fig. 179 is all that is required. If, however, such measurements are to be based on a strictly comparative method, a simple ebulliometer for cor-

Fig. 178

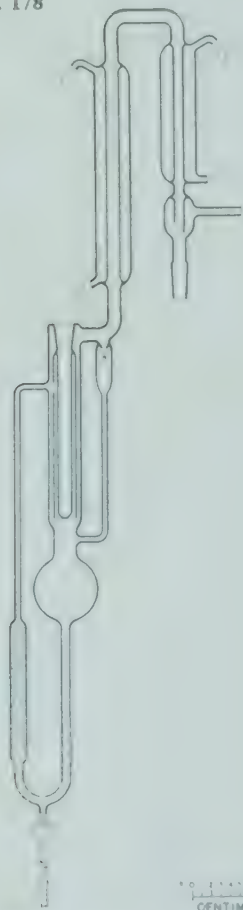
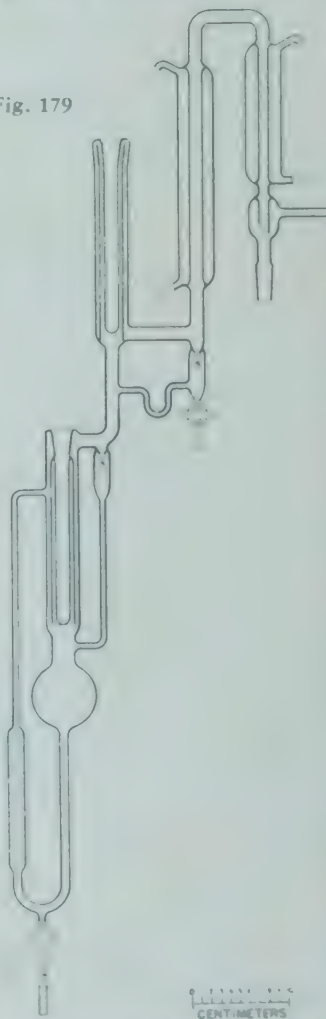


Fig. 179



recting the boiling and condensation temperatures, before and after the introduction of the solute, should also be employed. It is very rare for an organic solute to be completely non-volatile in the solvents ordinarily used. Indeed, the combined use of simple and differential ebulliometer allows the experimenter to obtain some idea as to the extent of this volatility and, further, allows him to choose as his standard a solute which has the same, or practically the same, relative volatility.

If a very small amount of the solvent, from which the solute was originally crystallized, or some moisture contaminates the solute, their presence may be detected if two ebulliometers are employed. Some solvents (e.g., benzene) very often used in molecular-weight studies are difficult to keep anhydrous during handling, and in addition their condensation temperatures are highly sensitive to moisture content. When

Fig. 180

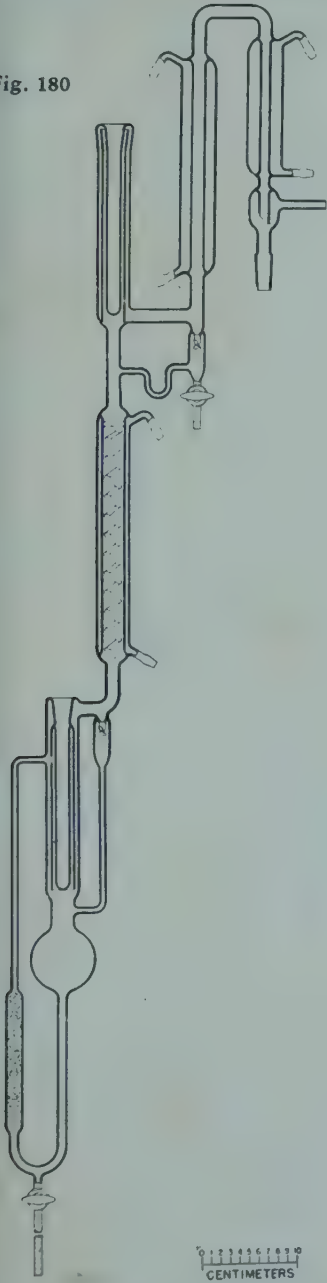


Fig. 181

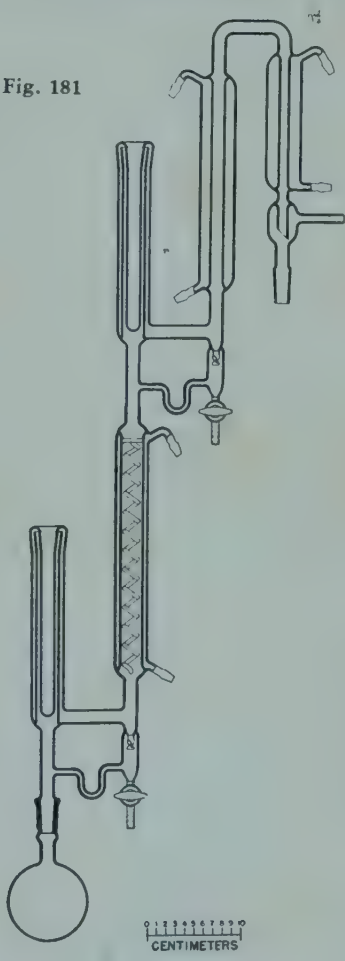


Fig. 182

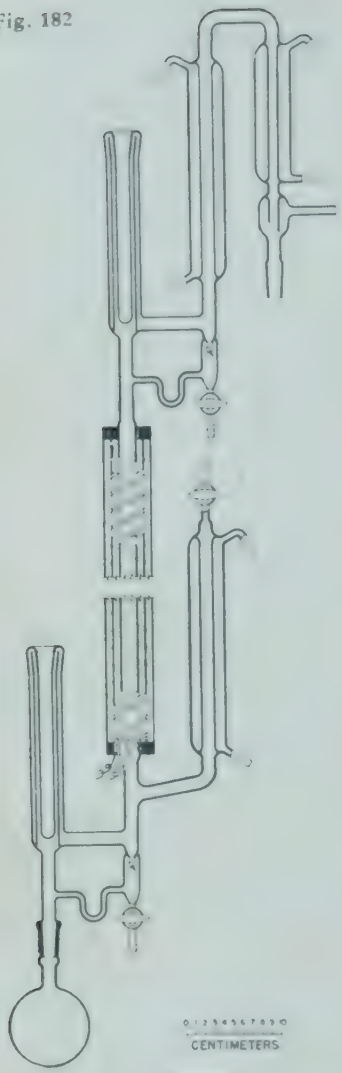


Fig. 183

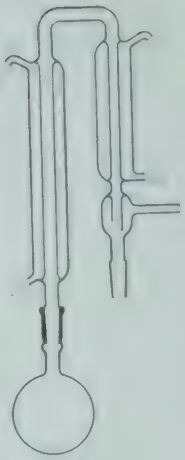
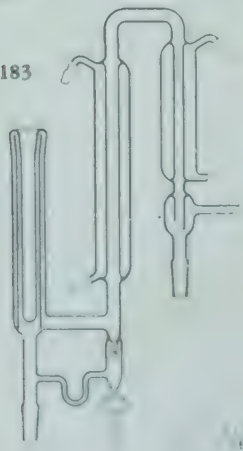
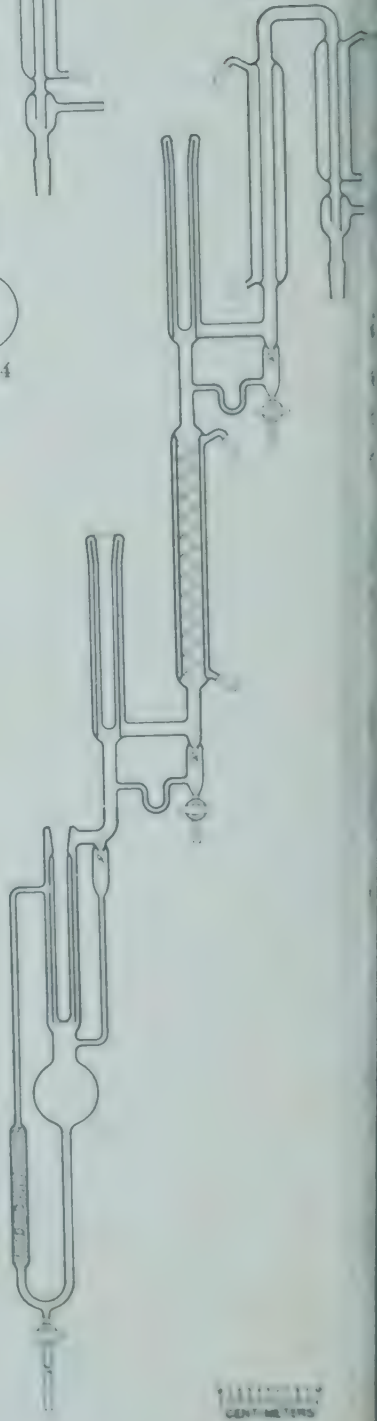


Fig. 184

Fig. 185



used in conjunction with a simple ebulliometer, the ebulliometer shown in Fig. 179 offers the possibility of detecting the slightest changes in moisture content of different portions of the same preparation of solvent. Furthermore, a relatively large volume of solvent is used in the differential ebulliometer, and, if necessary, an accurately-measured amount (containing practically all the moisture) can be removed *before* the solute is added. With benzene, or any other liquids forming heteroazeotropes with water, practically all the water can be removed by distilling off two or three milliliters. These advantages are not the least among those obtainable when ebulliometers of this type are used for molecular-weight work. It should be emphasized, however, that a less strict method of comparative measurements can be applied in molecular-weight work should only one ebulliometer—a differential one (Fig. 179)—be at hand.¹ Then, too, molecular-weight determinations based on the comparative principle can be made with two *simple* ebulliometers.¹

Where ebulliometers are constructed for those molecular-weight investigations which involve direct addition of solute to the solvent in the ebulliometer, it is necessary to seal onto the spherical reservoir of element A a side-arm with a ground glass stopper (similar to that adjoined to the pear-shaped reservoir as shown in Fig. 188).

For determining the ebulliometric degree-of-purity of a liquid substance or a homoazeotrope, a differential ebulliometer with a rectifying element C (Fig. 180), and a simple ebulliometer (Fig. 178) are required. For determining the ebulliometric degree-of-purity of heteroazeotropes, special devices which *cannot* be built from the standard elements here described have been recommended by Swietoslawski.

Fig. 181 shows an ebulliometer in which condensation temperatures, only, can be measured—one, *before*; and one, *after*, rectification of the vapors; it has been recommended¹ for examination of the purity of high-boiling liquids. The sensitivity of this device may be improved upon by replacing element C with a packed column (element F) as shown in Fig. 182. The lower part of this column should be equipped (as shown in Fig. 175 and 182) with a side-arm for holding an additional element E which is provided with a stopcock (element I). Measurements for this purpose in this device are made not simultaneously but alternately—first, before rectification and second after the vapors are passing through the column. Appropriate manipulation of the stopcock of element I, and of the coolant in the lower element E, makes these measurements possible.

Determinations of the degree-of-purity of liquid substances or homoazeotropes usually follow experiments in which relatively large amounts of the substance under ebulliometric

examination have been rectified in efficient columns. This is a consequence of the fact that, very often, so-called "heart cuts" from a distillation are not necessarily the purest samples from the cryometric or the ebulliometric point of view. In such work, a great deal of information regarding the nature of the impurities present can be obtained if the experimenter has a precise condensation-temperature curve for a large sample, as well as precise ebulliometric and cryometric degree-of-purity data on the various fractions. For precise measurements of condensation temperatures at the head of a distilling column, the device shown in Fig. 183, constructed from elements B, D and E, is to be recommended. The change in condensation temperature as a function of volume of distillate can be obtained to an accuracy of one or two thousandths of a degree when using this head in conjunction with a simple ebulliometer which contains a relatively pure sample of the substance under examination. Thus, for examination of the purity of substances by the ebulliometric method, a distilling column provided with the head shown in Fig. 183, a simple ebulliometer, and a differential ebulliometer for determining the ebulliometric degree-of-purity of the fractions are required. Usually, all of these devices should be connected to a common manostat so that, if desired, the operations can be carried out at a predetermined pressure and under an inert atmosphere. The same equipment is also to be recommended for use in studies of homoazeotropy.

The device shown in Fig. 183 has other important applications; for example, when equipped with a round-bottomed flask (element G) containing a reference substance, it can be used like a simple ebulliometer for correcting (for pressure fluctuations) the temperature found in an identical device acting as the head of a distilling column. It is also useful for drying certain liquids (such as benzene) azeotropically if it is desired to follow the progress of the operation by temperature measurements. If such measurements are not desired, an apparatus consisting of elements D, E and G, as shown in Fig. 184, suffices for drying the substances.

Fig. 185 shows a differential ebulliometer (composed of elements A, B, C, B, D and E) for molecular-weight determinations in which it is necessary that moisture be removed from the solute *after* the latter has been put into the apparatus. Swietoslawski has cited the interesting work of Centnerszwer and Lazniewski on the use of apparatus of this type where salts, which were practically impossible to dehydrate except by heteroazeotropic distillation, were the objects of the investigation.

Fig. 186 shows an especially sensitive differential ebul

liometer used for determining the degree of purity of ultra-pure liquids or homoazeotropes, or for microanalytical determinations of impurity-content.¹ Fig. 186 differs in principle from the ebulliometer shown in Fig. 180 only in that provision has been made for more efficient rectification of vapors. It is operated in a manner similar to that recommended for the ebulliometer shown in Fig. 182 (in order to eliminate corrections for the fall in pressure across the column packing).

Finally, a multistage ebulliometer for measurement of boiling temperature and condensation temperatures after varying degrees of rectification, is shown in Fig. 187. The rectifying elements in Fig. 187 may, with other suitable changes, be replaced by standard elements F. Such devices permit determination of the distribution, with regard to condensation temperature, of components of a liquid mixture.

Special ebulliometers, of use for examining amounts of substances smaller than would be mandatory if the standard element A were employed may be constructed by making smaller the spherical reservoir, and reducing the size of the activated cylindrical boiler of that element.

Unfortunately, there are two kinds of ebulliometers which *cannot* be constructed from the standard elements: (a) ebulliometers for measuring the boiling and condensation temperatures of two immiscible liquids, and (b) ebulliometers for examining liquids containing small amounts of highly volatile components.¹ The writers have neither constructed nor used ebulliometers of these types.

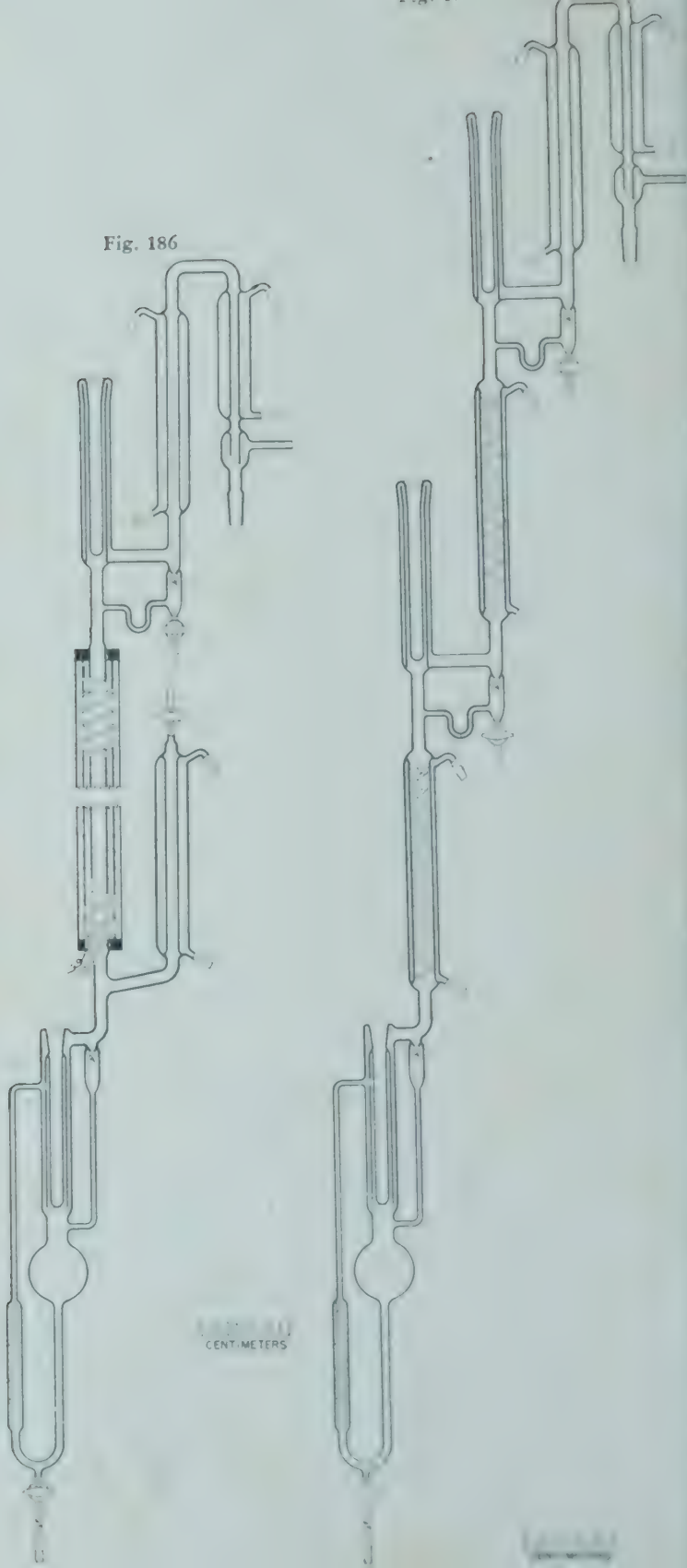
Removal of Moisture

If moisture is to be removed from the substance under examination by heteroazeotropic distillation, the condenser system consisting of elements D and E is operated in the following way: First, coolant is circulated in both D and E; second, when the moisture has accumulated in D, the coolant is removed from the latter and the vapors are allowed to rise until they are just condensing in E. Third, coolant is quickly reintroduced into D and the whole procedure repeated. Finally, coolant is removed from *both* D and E and, as soon as the vapor has penetrated all the way down to the receiver, coolant is quickly circulated, first through D, and then through E. The receiver (element H) may now be replaced by a drying tube. The whole operation, which may be repeated if necessary, usually requires the removal of two or three milliliters of the sample under examination.

Insulation

As a rule, it is desirable that the numbers of drops passing the drop counters located in the various parts of the apparatus should be the same or nearly the same. Usually, only a fraction of the heat-loss (through the insulation) can be

Fig. 186



compensated for by heating the U-tubes which return the condensate to the condensation-temperature elements. For this reason particular attention should be devoted to the problem of adequate insulation of ebulliometers, especially when the latter are differential or multistage, and where high-boiling substances are the objects of investigation. We prefer to use asbestos-paper tape* together with $\frac{1}{8}$ " asbestos cord† as the insulating materials. After having been soaked with water, the cord is wound on as the first layer; this is followed, successively, by two or three layers of tape, also water-soaked, by another layer of cord, and, finally, by another layer or two of tape. If the subjects of measurement are liquids boiling much above 100°C., it is advisable to insulate the boiling-temperature wells further and to wind some nichrome resistance ribbon onto the top layer of tape on the condensation-temperature wells and rectifying sections. The ribbon, which should also be covered with cord and tape, can be used as an auxiliary electric heater for the introduction, even during the measurements, of a predetermined amount of heat into the insulation.

After acquisition of the requisite minimum of skill, it becomes possible to wind the wet cord over the irregular parts of the apparatus in a *uniform* layer. For insulating such parts, however, it is convenient to work with short pieces of the cord.

Electric Heaters

Electric heating-wires should be wound around the cylindrical boiler of element A and around the left half of the U-tube of condensation element B, and, of course, any one of a variety of materials may be employed for this purpose. We prefer to use, in both heaters, Nichrome wire having a resistance of approximately four ohms per foot. About ten feet is usually required for the boiler of element A and about one foot for the U-tube. Both heaters should be connected to an ammeter and appropriate fuse, and should be controlled by an autotransformer. The resistance wire is first insulated with approximately $\frac{1}{16}$ " asbestos tubing* and then wound onto the boiler or U-tube. When winding the boiler it is more convenient to begin at the bottom (by looping the end of the wire under the first turn) and then winding upwards; the top end of the wire is then looped under the last turn. The tubing containing the resistance wire is then covered with several layers of asbestos-paper tape and, then with one or more layers of asbestos cord. Insulation should cover the entire boiler even though the resistance wire may not. For winding the U-tube, it is usually more convenient to start at the bottom of the U-bend: the asbestos tubing is

*Keasbey & Mattison Co.

†Johns-Manville, Inc.

covered by wet asbestos paper, only, and this is then molded with the fingers to the desired shape and thickness. It is scarcely possible to cover the U-tube heater with asbestos cord, owing to considerations of tube size and cord thickness.

The insulated boilers should be made first and then dried in an oven, before the elements are assembled. In this way, the boilers may be used for heating a liquid whose condensation will facilitate drying of the ordinary insulation.

Ebullimeters of the Original Swietoslawski Design

Many American investigators have used simple and differential ebullimeters based on Swietoslawski's *original* design for molecular-weight work and for obtaining dt/dp data by the comparative, dynamic method. Fig. 188 is a photograph of a pair of ebullimeters of this type—simple and differential, respectively—adapted especially for molecular-weight work. Element E (Fig. 185) may be used in conjunction with these devices. For collection of dt/dp data, the side-arm of the differential ebullimeter, and the stopcocks of both ebullimeters shown in Fig. 188, are usually removed and element E is sealed directly to the condensers. The thermometer-wells of these apparatuses have been built to accommodate either short-stemmed Beckman thermometers as modified by Swietoslawski, or platinum-resistance thermometers. The latter have usually been employed in dt/dp determinations.

B. CONSTRUCTION

The construction of ebullimeter elements and accessories for different ebulliometric arrangements is not difficult if the fundamental techniques of glass manipulation have been mastered. Basically, ebullimeters consist of four distinct parts, the boiler, thermometer well, condenser and the condensed liquid drop counter. It will be helpful to describe the construction of the above parts in order to point out details which require critical attention.

The Boiler

The production of a boiler which will give smooth boiling with a minimum of superheating is essential in any apparatus in which the boiling of a liquid constitutes the major operation. Even though smooth glass surfaces are employed in the majority of cases, such surfaces cannot be expected to give smooth boiling. Activated boilers can be made quite easily by fusing small glass particles to the boiler surfaces. Small capillary cavities which are formed in this sintering process serve as active points for vapor formation and consequently smooth boiling is obtained with a minimum of superheating.

Powdered glass, 50 to 60 mesh, is required for producing activated boiler surfaces. This glass must have the same

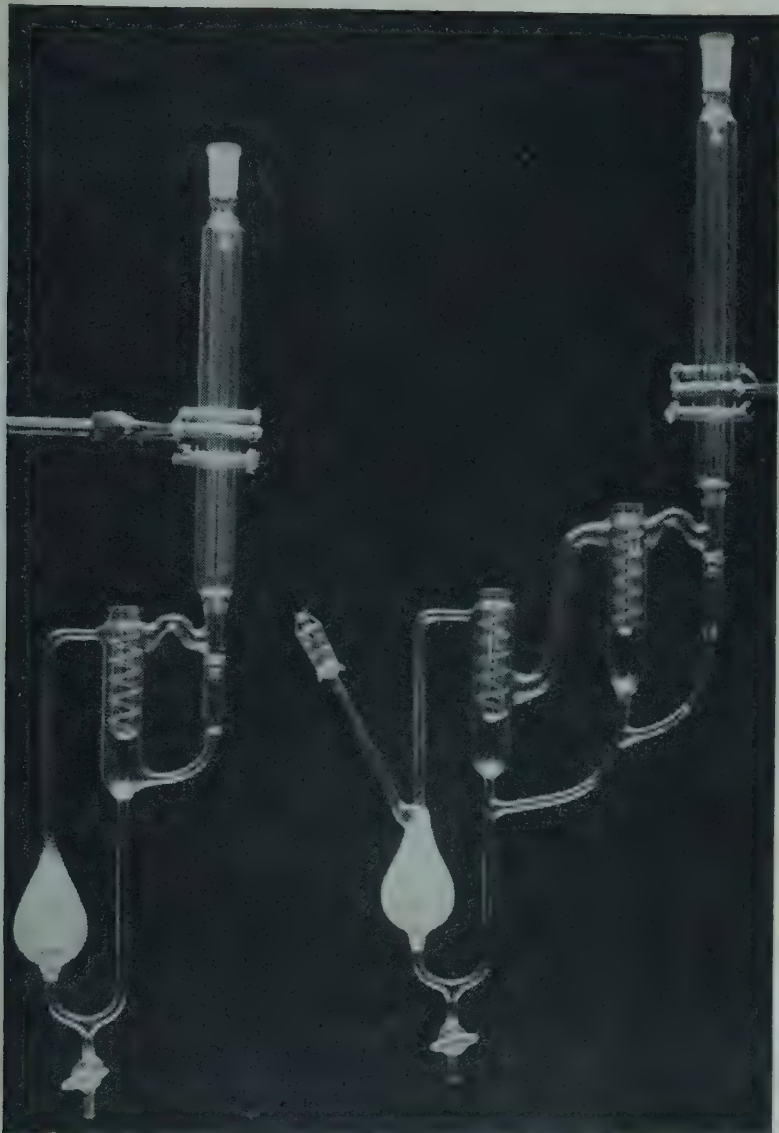


Fig. 188

composition as that of the boiler. The powdered glass is obtained by first breaking a glass tube into glass chips. These chips are pulverized in a disk mill or an iron mortar and pestle. The pulverized glass is then screened to 50 to 60 mesh. Iron particles are removed with a magnet before the pulverized glass is used.

Sintered Glass Boilers

Sintered cylindrical glass boilers are made as follows:

1. A cylindrical boiler with the shape and dimensions

shown in Fig. 175A is filled with 50 to 60 mesh glass. This glass is held in the boiler by two glass wool plugs. The packed tube is then chucked in a lathe and the boiler is progressively heated from one end to the other. It is important to heat the tube to the temperature which will just fuse the pulverized glass to the boiler tube. If the tube is heated too hot, the edges of the small glass particles will become smooth and the powdered and fused glass will collapse, closing the small capillary cavities. The remaining loose glass powder is removed and the boiler is then annealed. If a lathe is not available, the operation can be completed by using supporting rollers.

2. Pear-shaped boilers for the ebulliometers shown in Fig. 188 are sintered by using just enough 50 to 60 mesh glass to cover the required surface in the boiler bulb. This pulverized glass is poured into the boiler which is then heated and rotated in a burner flame. As it approaches red heat, the loose powdered glass in the bulb will stick to the walls. A uniform coating of the small glass particles is obtained by rotating the boiler to build up the desired layer of sintered glass. Again, it is important to heat the boiler to the temperature which will just fuse the glass particles to the surface.

Thermometer Well Construction

Three different forms of thermometer wells have been illustrated in the ebulliometer elements discussed in this article. The length of the wells will depend on the thermometer which is to be employed. Construction details, however, are the same regardless of the size of the well.

The thermometer well of the element in Fig. 175A consists of the well with a tapered open end, a baffle tube and the outer jacket. The well is made by first closing one end of the tube. The open end is then reamed to shape with a standard taper. The depth and size of the taper will depend on the size of stopper to be used on the thermometer. All tapered ends should be the same size. The end of the taper is spun into a flare for the flare seal. The well is then ring-sealed to the baffle tube and a liquid and vapor inlet hole is blown into this tube below the ring seal. The well and baffle tube are then centered in the outer tube and held in place with glass tape pads. The flare seal is made. The glass at the tapered end is periodically tooled with the standard taper during this operation. Immediately after the flare seal is completed, the vapor outlet tube is sealed to the outer tube exactly opposite the liquid and vapor inlet in the baffle tube. The flare and vapor tube seals are then annealed.

The thermometer well, Fig. 175B, is constructed so that the vapor passes up between the thermometer well and the

barrel tube and then downward through the annular space between the barrel and outer tube. In this case the tube of the well, the barrel tube and the tube of the outer jacket are all tapered. A flare is spun at the open tapered end of the thermometer well. The barrel tube is ring-sealed to the outer tube. The tapered end of the barrel tube should be about 5 mm. below the end of the outer tube. The side arm is sealed to the outer tube as soon as the ring-seal is completed. The glass is then annealed at these seals. The thermometer well is then centered in the element and the flare seal is made and annealed.

The thermometer wells in the ebulliometers shown in Fig. 188 differ from those previously discussed in that a glass spiral is fused to the well. This spiral favors better thermal equilibrium between liquid and vapor because the liquid on the thermometer well must flow along the spiral.

The thermometer well is made as follows:

1. Points are pulled on both ends of the tube which is to serve as the well. A shoulder is blown on this tube for the ring seal. A 5-mm. glass rod is then fused to the tube just below the shoulder. The tube is turned with the point held in the left hand. The rod is heated with a burner flame and as it becomes pliable it is wound around the tube. The spiral should touch the well at all points. When the desired spiral length is obtained, the rod is fused to the tube and the excess glass is cut with the burner flame. Immediately after this operation, sections of the spiral are heated white hot progressively from this point until it is fused to the well. It is important that the rod be heated only to cause fusion at the point of contact on the tube; the rod should not be deformed in any way or the maximum liquid exposure area will not be obtained. A blow-tube on the point held in the left hand is used to blow out the glass in the well should it be accidentally collapsed. The tube at the end of the spiral is then cut and closed. The well is then annealed.

The well is sealed into the outer tube by the procedure illustrated in Fig. 41. The two side arms are then immediately sealed to the outer tube.

Drop Counters

The construction of drop counters has been previously described and illustrated in Fig. 43. The drop counters in all elements should be as near alike as possible. The maximum diameter of the glass hemisphere should be 8 mm. The flat plane of the hemisphere should be perpendicular to and centered in the counter tube.

Assembly of Ebulliometer Elements

The ebulliometer elements are assembled either by sealing together the tubes of the desired elements or by using ground

glass joints. The former method of assembly is recommended because of the disadvantages of using ground joints without lubricants. The elements are assembled by clamping them to a rack and sealing them together with a hand torch. If ground joints are used, they should be of the No-Lube type.

DESIGN AND CONSTRUCTION OF
DISTILLATION EQUIPMENT

The advancement of the distillation art in the last twenty years has been very encouraging. The development of packing for fractionating columns, along with new techniques and construction details, has made it possible to separate complex mixtures both on a commercial and laboratory scale. Research chemists find that fractionating columns can be advantageously used to purify compounds for chemical synthesis. The problem of identifying synthesis products is also simplified. The cost of setting up such columns need not be high. In fact, with a little ingenuity, a simple fractionating column can be set up in the laboratory at a reasonable cost. The improved commercial columns have also decreased the cost of many chemicals. These chemicals which have a relatively high degree of purity are now available in tank car lots.

A discussion of the entire distillation art cannot be given, nor will it be necessary to discuss commercial installations. It will suffice to describe equipment which is used in the laboratory, with special emphasis on construction details.

A discussion of laboratory distillation columns should logically cover the entire range of separations which are encountered in the laboratory. To accomplish this end, it will be necessary to divide the equipment into the following four groups:

1. Fractionating equipment for separating normally gaseous compounds.
2. Fractionating equipment for separating compounds with boiling points at atmospheric pressure up to 250°C.
3. Vacuum fractionating equipment.
4. Molecular or short-path distillation equipment.

The development of equipment listed under 1, 2 and 4 has greatly surpassed the development of vacuum fractionating equipment. Recent research trends have shown that this equipment is in demand and is certain to receive attention in the future.

The division of fractionating equipment into these four groups does not imply that the equipment is restricted to its respective group. A certain amount of flexibility is possible. It should be pointed out, however, that there are definite limitations of laboratory columns in each group. Laboratory technicians should be aware of the shortcomings

of columns when they are used under different operating conditions.

DEFINITION OF DISTILLATION TERMS

A discussion of distillation equipment can best be understood if one is familiar with the terminology used. The terms which will be used in this discussion are as follows:

1. *Stillpot.* The flask or container in which the charge is vaporized.

2. *Boil-up rate.* The amount of charge vaporized in the still pot in unit time.

3. *Packing support.* Support in the column which holds the packing in place.

4. *Height of Fractionating Section.* Height of packing or bubble plate section in column. A small amount of fractionating is obtained in the condenser and vapor tube leading to the condenser as well as between the stillpot and column. The term as used here will apply only to the length of the packed column.

5. *Packing.* Inert material in the fractionating section which permits intimate contact between vapor and liquid by virtue of its surface area.

6. *Free Space.* Space in fractionating column not occupied by packing. This void space can be determined by filling a graduated cylinder to the zero mark with packing and determining the void space by adding a non-volatile liquid. The volume of this liquid required to fill the graduate to the zero mark is the free space.

7. *Vapor velocity.* Linear velocity of the vapor through the fractionating column. Space occupied by reflux and packing material is neglected when vapor velocity is calculated.

8. *Hold-up.* The operating hold-up of a distillation column is the amount of liquid and vapor in the distillation column when the column is being operated. The amount of liquid that does not drain from the column when operation has ceased is the static hold-up.

9. *H.E.T.P.* The height equivalent to a theoretical plate.

10. *Theoretical Plate.* A plate in which the ascending vapor in the column contacts the liquid so completely that all vapor is in equilibrium with the liquid.

11. *Pressure Drop.* The pressure drop is the difference in pressure between two points in the fractionating section, usually between the bottom and the top of this section.

12. *Total Still Head Condenser.* The part of the distillation column where all vapors from the fractionating column are condensed.

13. *Partial Still Head Condenser.* The part of the distillation column where a portion of the vapor from the fractionating section is condensed and returned to this section. The remaining vapor is condensed in a second condenser and removed as product.

14. *Reflux.* Condensed vapor which is returned to the fractionating section.

15. *Reflux Ratio.* The ratio of the amount of liquid returned to the fractionating section and the liquid removed at the condenser as the distillation product.

16. *Total Reflux.* Total return of the condensed vapor to the fractionating section.

17. *Batch Distillation.* Process in which a definite amount of

liquid is charged to the stillpot. This liquid is vaporized and condensed into fractions, each of which may vary in composition.

18. *Continuous Distillation.* Liquid is charged to the column at a definite rate. Several products are removed from the column. The composition of each product is different from the others, but in itself has a constant composition.

19. *Rectification.* A distillation process where the condensate or reflux is brought into intimate contact with the ascending vapors causing a heat and material change between the two phases. The vapors are enriched in the more volatile components by the heat exchange, and consequently, the liquid phase is enriched in the less volatile components.

OPERATING REQUIREMENTS OF A FRACTIONATING COLUMN

A theoretical discussion of the rectifying principle of separating various components in a mixture need not be given. A thorough treatment of the theory of distillation and vapor-liquid equilibria data can be found in numerous articles covering the art of distillation. The design and construction of fractionating equipment does demand a certain amount of knowledge concerning the function and operation of the column. Certain requirements must be set up for satisfactory column operations. The degree in which these requirements are met will determine to a great extent the operating efficiency of the fractionating column. These requirements are as follows:

1. A constant and uniform vaporization must take place in the stillpot.
2. The rectifying section of a column must be adiabatic.
3. Intimate contact between descending liquid (condensate from the still head condenser) and the ascending vapors from the stillpot is necessary.
4. Adequate and constant reflux must be maintained to the rectifying section.
5. Means must be provided for dividing reflux and the distillate product.

The importance of a uniform boil-up rate in the stillpot has received very little attention in fractionating columns. These columns operate on the principle of establishing equilibrium between the vapors and liquid in the fractionating section. Uniform vapor flow is more advantageous than uneven flow. To obtain a uniform vaporization rate, consideration must be given the stillpot surface as well as the method of heating the stillpot. A method of maintaining a more uniform vaporization will be discussed under the description of the stillpot.

Fractionating columns should be adiabatic because of the equilibrium desired between the vapors and reflux in the column. Lateral heat flow from the column cannot be tolerated if very efficient rectifying columns are required. All heat exchange should take place between the two phases

in the column and not with the column walls. Excessive heat loss in small sections will cause condensation which favors flooding of these sections. The attainment of equilibrium cannot be expected under these conditions. On the other hand, if too much heat flows into the columns from the outer wall, i.e., if heaters are placed on the wall, heat exchange between the two phases alone cannot be obtained. Vaporization will result, depleting the column of scrubbing liquid. Various methods for approaching adiabatic conditions in laboratory columns will be discussed in another section of this chapter.

The fractionating section of a column may be viewed as a number of consecutive simple distillations. Vaporization and condensation takes place in this section by virtue of the heat and material exchange between the liquid and vapor phases. High boiling components are scrubbed from the ascending vapor and low boiling components in the reflux or liquid are vaporized by the heat released by the condensing process of the high components. The extent and rate to which this interchange of heat condensation and vaporization takes place depends on the intimate contact of the two phases. Numerous column packings have been studied and results of some of these studies will be given under column packings.

The importance of maintaining adequate reflux need not be stressed in view of the discussion in the preceding paragraph. The column when operating under specified conditions will approach the equilibrium which is possible at the predetermined conditions. If the reflux ratio is low, very little rectification can be expected due to lack of adequate scrubbing action in the column. If the reflux ratio varies during the distillation, a variance in the equilibrium of vapor and liquid will be obtained, and consequently, the degree of rectification must change.

The removal of distillate must be controlled. The reflux ratio has been defined as the ratio of the amount of reflux returned to the column and the amount of product taken from the column. If the removal of the product cannot be controlled, the column equilibrium will be affected in the same manner as a change in the reflux ratio.

THE DISTILLATION COLUMN

The Stillpot

The round-bottom flask is the common form of stillpot for laboratory fractionating columns. This flask is sometimes sealed directly to the column. The use of the ground glass joint, however, is the most common method of attaching the stillpot to the column. The spherical ground glass joint has gained considerable favor over the tapered joint because the latter is likely to freeze under some op-

erating conditions. The spherical joint can be used to good advantage if it is carefully cleaned. A certain amount of flexibility is obtained since the still pot need not be exactly in line.

The stillpot should be of suitable size to accommodate the charge and should contain a thermowell. The liquid in the stillpot can be overheated especially if high boiling components are present in the charge.

A tube, sealed to the stillpot above the liquid level, is also required if a manometer is used to measure the pressure drop through the column. A spherical joint sealed to this tube obviates the danger of subjecting the side tube to tension when the connecting tube between the stillpot and manometer is not perfectly aligned, Fig. 189.

The method by which the stillpot is heated to give even boiling does deserve some consideration. Several ways of heating the charge in the stillpot are: by use of an open electric heater, a gas flame, a heated oil bath, or an electrical heater enclosed in a metal container which fits around the stillpot. The use of some of these heaters should be discouraged. The glass-cloth-covered electric mantles sold by the Glas-Col Apparatus Company of Terre Haute, Indiana, are very good. These mantles allow exact heat input by using a voltage-regulating transformer such as the Powerstat or Variac. They cover the entire stillpot, eliminating the danger of breaking the flask and can be purchased for any flask size. These mantles are light. They can be supported by special spring supports which hold the stillpot and column joints together with the desired tension. Linear expansion of the column is possible because of the springs.

The problem of heating the charge in the stillpot so that a minimum amount of superheating is obtained is not readily solved. It has been noted that a more uniform boiling rate is obtained if the inside wall of the stillpot is coated with small glass particles of 50 to 60 mesh size. These particles are partly fused to the flask in the following manner: A portion of powdered glass, (Pyrex 774) of 50 to 60 mesh, estimated to cover the wall of the flask (Pyrex 774), is poured into the clean flask. A suitable holder is then fastened to the flask opening. The flask is slowly and uniformly heated in a large flame until the powdered glass begins to cling to the inside surface. At this point the flask is heated and rotated in such a manner to give a uniform coating without fusing the powdered glass to the extent that the surface becomes transparent. When an opaque and uniform surface is obtained the flask is carefully annealed and allowed to cool.

Immersion heaters with low heat capacities are also being used for heating the charge in the stillpot. These heaters

have the advantage of low heat capacity and immediate response to electrical current changes. They must extend to the bottom of the stillpot if all material is to be distilled. Side-arm openings or glass-to-metal seals in the flask are required when such heaters are used.

Pressure Drop Control

The pressure drop through the packing of a fractionating column is a measurement of the boil-up rate. Since it is necessary to maintain a constant reflux ratio in precision

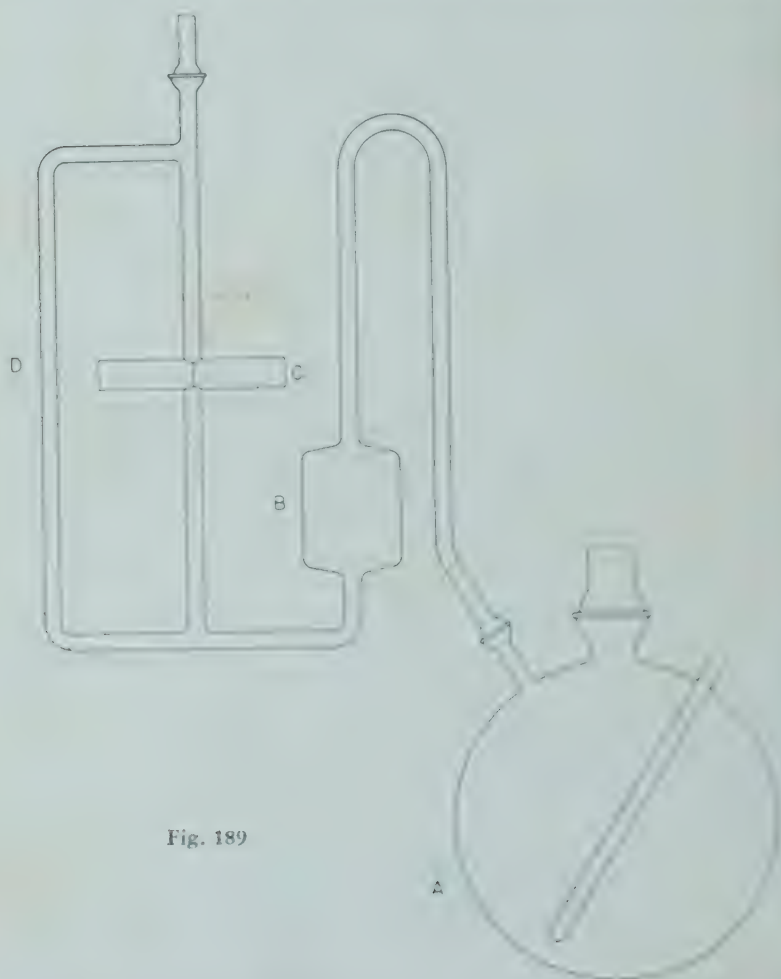


Fig. 189

fractionation, some means must be provided for the control of the boil-up rate. A manometer connected to the stillpot and condenser, or to the stillpot alone if distillations are made at atmospheric pressure, will indicate the pressure drop across the packing. This pressure drop can be held fairly constant by manual control of the heat input to the

stillpot. Such an operation is tedious. Numerous manostatic controls have been used to control the boil-up rate.^{1,2,3} One assembly which has been successfully used is shown in Fig. 189. The manometer consists of a wide and narrow leg, B, D, the former being connected to the stillpot. A short section of rubber tubing in the connecting line will increase flexibility. A light source and phototube are housed in the two tubes, C, which converge on the narrow leg. The third leg is useful for visual observation. The manometer is filled with dibutyl phthalate colored with the dye Nigrosine.

The phototube circuit need not be discussed. Numerous small and compact commercial units are available. The "Model 150" unit produced by United Cinephone Corporation is suitable. The circuit described by N. Ceaglske and S. Kesslinger⁴ can also be used. Use of the "1P42" phototube produced by Radio Corporation of America makes it possible to mount the tube in a small space. This phototube is only $1\frac{1}{4}" \times \frac{1}{4}"$. Its screen is perpendicular to its axis and can thus be mounted in a small short Bakelite tube. The phototube and light source should be perfectly aligned and mounted on a single slide rod. A small thumb-screw can be used to hold the entire assembly in the desired position.

The circuit for the stillpot heater is quite simple. It is necessary to have it arranged so that a portion of the current is cut off when the boil-up rate is too high. A power source connected through the relay in the photoelectric circuit is used to supply current to the coil of a heavy-duty single-pole double-throw relay.

The heater current is obtained from the load side of a variable-voltage transformer such as a Variac or Powerstat. One of the load lines is connected to the stillpot heater. The other line is connected to the movable contact of a heavy-duty relay. The two fixed points on the relay are connected to the stillpot heater through two separate lines. One of these lines contains a resistor. When the boil-up rate is too high the phototube is cut off from the light source. The relay in the phototube circuit is energized, which in turn energizes the heater relay. The heater current is then cut down because of the resistor. This will cause a drop in the boil-up rate which in turn gives a decrease in the pressure drop. The phototube is energized by the light source when the pressure drop decreases and the heater relay is de-energized. A greater current is then supplied to the stillpot heater. This current is adjusted by the Variac or Powerstat to give a boil-up rate which is just slightly greater than the required rate.

A second method of controlling the pressure drop in

fractionating columns operated at atmospheric pressure is the use of an open-end manometer. This manometer has a wide leg and a narrow leg which is open to the atmosphere. The manometer is charged with diethylene glycol colored by the dye Negrosine. A small amount of sodium nitrate is dissolved in the diethylene glycol to increase the electrical conductance of this manometer fluid. Two insulated probes are used in the narrow leg for the actuating contacts for an electronic relay which controls a heater exactly as described for the phototube assembly. Commercial electronic relays are available. The General Electric relay "CR7511-A111" is satisfactory. The conductance of the diethylene glycol-sodium nitrite mixture is sufficient to operate the electronic relay. One of the probes is set about $\frac{1}{16}$ " below the other at the desired pressure drop level. The control level is between the two probes. When the pressure rises to the top probe, the heater current to the stillpot is cut down to give a lower boil-up rate and when the manometer fluid level is below the top probe, the heater current is sufficient to give a higher boil-up rate.

Methods of Making Columns Adiabatic

The problem of making a small laboratory fractionating column adiabatic is one that does not lend itself to an easy solution. If compounds with greatly different boiling points are fractionated, a large temperature gradient is obtained between the bottom and the top of the column. On the other hand, if compounds with close boiling points are to be fractionated, the temperature gradient will be quite small. Usually a fractionating column is designed for one specific mixture. However, a great deal of flexibility is desired and often required. Consequently, columns for general use should at least approach adiabatic conditions under such operations. To obtain such conditions, heat must be supplied to small laboratory columns. Electrical heaters can be arranged to give approximate adiabatic conditions.

The vacuum-jacketed column which is silvered or contains a radiation shield,⁵ probably is the most effective method of making an adiabatic laboratory fractionating column. However, even with a vacuum column, some heat is lost especially if compounds are distilled which have boiling points in the range 150 to 250°C. To minimize this heat loss an electrical heater can be wound around the outer jacket. Such an arrangement is illustrated in Fig. 190B.

Thermocouples are fastened to the outside of the vacuum jacket by covering them with a thin copper sheet and wiring this sheet to the jacket. The thermocouples should be spaced along the length of the jacket, especially if more than one column heater is used. A layer of asbestos sheet or

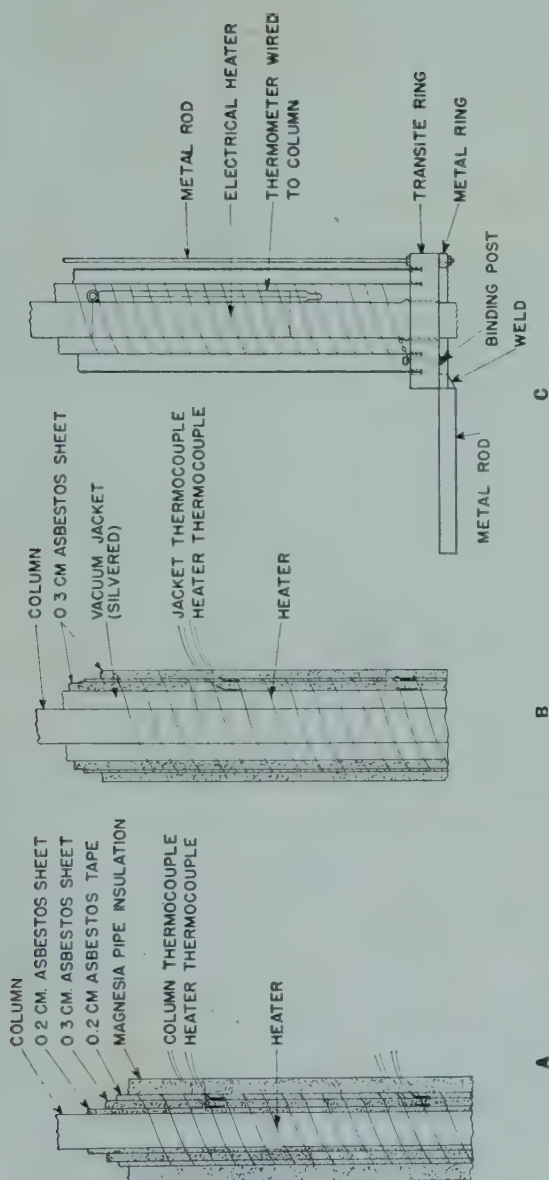


Fig. 190

tape is wrapped over the jacket to a thickness of about 0.3 cm. A second set of thermocouples is fastened directly over the first set by the procedure outlined for the first set. A double layer of asbestos tape or thin asbestos paper is wrapped on the column over the thermocouples. A suitable resistance heater is then wound on the covered jacket. If a large temperature gradient is expected when the column is

in operation, the heater windings on the jacket can be spaced so that more heat is supplied to the bottom section. An alternative is to use two or more separate heaters along the length of the column. The heater is covered with a 0.3 layer of asbestos paper or tape.

The thermocouples, one next to the jacket, and the second under the heater, are used to indicate whether that portion of the column is operating under adiabatic conditions. If both indicate the same temperature, there is no lateral heat flow.

It is sometimes necessary to use the insulation, thermocouples and electrical heater directly on the column. This method is illustrated in Fig. 190A. The arrangement of thermocouples, lagging and heater is similar to that of the vacuum jacketed column except that the column is first wrapped with asbestos paper or tape and magnesia pipe insulation is used as the final covering.

A third method, frequently used, is illustrated in Fig. 190C. This arrangement is advantageous when complete visibility is desirable. The column is surrounded with an air space. Thermometers or thermocouples are wired to the column. The heater tube should be large enough so it can be slipped over the column. Small holes at each end of the tube are used to anchor the heater. Three lengths of asbestos cord, $\frac{1}{8}$ " in diameter, extend along the entire length of this tube. The electrical heater is wound on the heater tube over these cords. The third tube is used to protect the heater. The two tubes and column are held in place by transite rings. Binding posts and metal column supports are fastened to these rings. Small rods hold the two end rings together.

The arrangement of a staggered dual heating element has been suggested by F. Todd.⁶ The top and bottom heaters extend the entire length of the jacketed space around the column and overlap at the middle third of the jacket. The upper and lower heaters are separated from each other by porcelain rings. Springs on these rings keep the heaters from sagging when the heater wires expand.

The choice and arrangement which is adopted for making a column adiabatic will depend on the facilities available. Vacuum-jacketed columns can be made in a good glass-blowing shop, but will require time for construction, silvering and evacuation. Voltage controllers are required for electrical heaters. Each addition of equipment for better control naturally complicates the distillation equipment. A complete study of what is required to do the job in the simplest way is always helpful before the apparatus is assembled.

Laboratory Column Packings

The function of the packing in a fractionating column is

to provide a medium for intimate contact between ascending vapors and the descending liquid or reflux. The packing should not materially reduce the throughput or capacity of the column. To facilitate contact of vapor and liquid, the packing should have a large surface area and at the same time have a high void space to allow vapor to move through the fractionating section.

Since packing is used to favor intimate contact of liquid and vapor, some means must be available to determine its efficiency. This efficiency is rated as the height equivalent to a theoretical plate or the height of the column in which the vapor in the column contacts the liquids so completely that equilibrium is established between the vapor and liquid. This height equivalent to a theoretical plate, H.E.T.P., is the basis upon which packings have been compared to date. Furthermore, the H.E.T.P. is an important factor when close boiling compounds are to be separated by fractionation.

The procedure in determining the H.E.T.P. of a packing is to operate the column under idealized conditions, i.e., total reflux, and at several different reflux rates. The column is first flooded and then allowed to operate under each of these conditions until equilibrium is established. Data from the analysis of the distillate and stillpot liquid are used to calculate the theoretical plates of the column. Data obtained under these idealized conditions are helpful mainly as a comparison of various packings. The reader is warned not to extrapolate data obtained at total reflux to operations at finite reflux ratios. Erroneous conclusions are often obtained by such procedures. It does follow, however, in the majority of cases, that packed columns which have a large number of theoretical plates under ideal operations are more efficient under operation of finite reflux ratios, than packed columns that exhibited fewer theoretical plates under total reflux.

To insure proper separation at finite reflux ratios, it is best to test the column under the desired operating conditions. F. C. Collins and V. Lantz⁷ have used such a procedure in their evaluation of the Oldershaw glass bubble plate column. It would be helpful if data as given by Collins and Lantz were available for all laboratory packing. Such data would reveal packing performance which would more nearly approach conditions used in the laboratory. Manufacturers of packings are eager to sell theoretical plates and consequently submit data which shown the smallest H.E.T.P. for their packing.

Selection of Packing for Laboratory Columns

Four factors must be considered when packing is selected for laboratory fractionating columns. These factors are as follows:

1. *The Height Equivalent to a Theoretical Plate.*

The choice of the H.E.T.P. will depend on the separation that is desired. The cost of very efficient packing (small H.E.T.P.) is considerably more than for less efficient packing. Consequently, if a low H.E.T.P. is not required, a considerable saving can be effected by choosing the less expensive packing. The available height for the column sometimes requires that a more efficient packing be used.

2. *The Pressure Drop Through the Packing*

The pressure drop through a packing must be considered when the fractionating column is to be used under reduced pressure. Since reduced pressure is employed to lower the boiling temperature of components in a mixture, it is essential to have a low pressure drop through the packing. Temperatures in the stillpot will not correspond to the recorded values which can be obtained under the reduced pressure at the top of the column.

3. *The Maximum Rate Without Flooding*

The maximum counterflow rate of vapor and liquid in a column, i.e., rate of flow just short of the flood point, determines throughput of the fractionating column. This rate should be large enough to be practical and yet not decrease the H.E.T.P. If time is not a factor in fractionations, low throughput rates can be tolerated provided the desirable H.E.T.P. can be obtained under such operating conditions. Some packing material exhibits changes in H.E.P.T. as the throughput is increased. These factors must be balanced against each other if a choice of packing is made.

4. *The Liquid Hold-up on the Packing*

If sharp separations are desired in fractionating a mixture, the operating hold-up must be small. The most important effect of hold-up is in its relation to the amount of the charge and the amounts of components in the mixture. More efficient fractionation can be obtained when the hold-up is small because more surface is employed to rectify one component in the charge. The development of efficient column packing has favored columns with low hold-up because shorter columns can be used.

A factor which is not related to the geometric design but which is very important, especially if a fractionating column is used as an all-purpose column, is to have packing which resists corrosion. Corrosive materials can then be fractionated. Of greater importance is the ease by which columns can be cleaned. Fouled packing cannot be expected to operate satisfactorily because the contacting efficiency is decreased. If the packing is resistant to corrosion, a cleaning solution (concentrated sulphuric acid and sodium di-

chromate) can be used. A *rapid* water wash of the packing is recommended after the packing is cleaned with the acid solution. Columns containing stainless steel carding teeth have been cleaned in this manner many times in this laboratory.

Many types and forms of packing as well as methods for effecting fractionation have been used. Considerable data can be collected from the literature concerning the H.E.T.P. of packing at different reflux rates. The trend has been toward the ideal packing, i.e., low hold-up, high capacity and low H.E.T.P. The H.E.T.P. and throughput data of some column packing recorded in the literature are given in Table 24. The column packings are divided into the following groups:

1. No packing.
2. Dump-in types.
3. Geometric types.

The data in Table 24 should be taken as a guide for the adoption of column packing. If any single packing is desirable, reference should be made to the original publication for a more complete discussion.

CONDENSERS

Since reflux is required in the operation of a fractionating column, some means must be provided for dividing vapors or condensed vapors which issue from the rectifying section. Numerous ways and methods have been tested and reported in the literature. Each of these column heads can be divided into two distinct types, the partial and total condenser stillheads. The former type, although used in some laboratories, does not have the popularity of the total condenser. It is more difficult to control the reflux ratio with a partial condenser. The total condenser, where the vapor or liquid is divided into reflux and product, is almost entirely used on small laboratory columns. The following discussion will be concerned only with total condensers.

The design of the stillhead should be simple. If the column is used in routine analysis, it is desirable to have simple stillheads which can be quickly and easily repaired when breakage occurs. Of greater importance in the design of the stillhead is a low hold-up capacity. The hold-up of the packing usually is high enough that considerable hold-up in the head cannot be tolerated. Another minor factor in the design of stillheads is that the vapor volume or void space between the packing and cold condenser should not be large.

The methods by which the overhead liquid or vapor stream is divided into reflux and product are as follows:

1. Manual operation of stopcock or tapered plugs.
2. An electrical cycle timer which operates a solenoid

TABLE 24

LABORATORY COLUMN PACKING

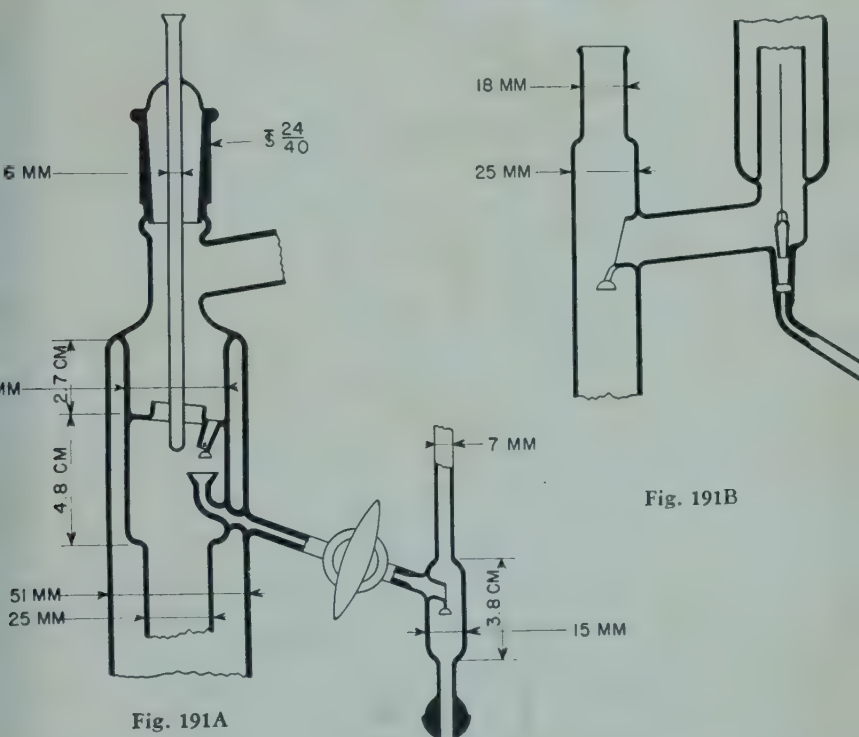
Type of Packing	Reference	Operation	Length of Column, Cm.	Diam. Reflux of Col. Rate Cm. cc/hr.	H.E.P.T. cm.	in.	Test Mixture	
1 No packing	8	Total Reflux	128	0.415	250	16	6.3	n-heptane-methyl cyclohexane
	9	Total Reflux	68.5	1.9				Benzene-carbon tetrachloride
	10	Total Reflux	30.3	0.3	36	3.36	1.32	Benzene-carbon tetrachloride
					180	30.3	11.9	Benzene-carbon tetrachloride
2 Dump-in Types	11	Total Reflux	290	5.1	2900	65	25.5	n-heptane-methyl cyclohexane
	12	Total Reflux	140	2.58	900	4.2	1.65	Benzene-ethylene chloride
	13							
	14	Total Reflux	68.6	1.9		3.2	1.25	n-heptane-methyl cyclohexane
Berl Saddles 4 × 4 mm. 7/32" Carding Teeth	9	Total Reflux	107	1.4	3800	9.5	3.7	n-heptane-toluene
	9	Carding Teeth	168	2.03	1500	7.62	3.0	Benzene-carbon tetrachloride
	10	Total Reflux	30.3	0.6	216	9.3	3.6	Benzene-carbon tetrachloride
	11	Total Reflux	290	5.1	14700	6.4	2.5	n-heptane-methyl cyclohexane
1/8" Carding Teeth	15	Total Reflux	150	3.15	4600	5.1	2.0	Benzene-ethylene chloride
					14800	8.9	3.5	
	16	Total Reflux	274	3.2	1800	7.4	2.9	n-heptane-methyl cyclohexane
					2100	5.6	2.2	
4 × 6 mm. Carding Teeth					5000	7.9	3.1	
Chain								
No. 19 Al Jack Chains		Total Reflux	150	3.15	3700	10.7	4.2	Benzene-ethylene chloride
					14000	13.7	5.4	Benzene-ethylene chloride
	12	Total Reflux	140	2.58	1290	3.5	1.3	Benzene-ethylene chloride
	15	Total Reflux	150	3.15	2200	5.1	2.0	Benzene-ethylene chloride
Commercial Materials								
					3700	4.6	1.8	

Perforated Plates	25	Total Reflux	45	3.2	1020 4500	2.9 4.5	1.14 1.76	Benzene-carbon tetrachloride
Spinning Band								
6 mm. Monel Band	26	Total Reflux	545	0.67	162	8.0	3.1	n-heptane-methyl cyclohexane
Rotating Cones	27		56	5.08	108	8.7	3.4	n-heptane-methyl cyclohexane
Spirals					282	9.5	3.7	
Square Threads on								
Monel Rod	28	Total Reflux	320	2.5	90 400 600	2.7 3.4 3.8	1.05 1.35 1.54	n-heptane-methyl cyclohexane
Wire Gage								
Stedman 105	29	Total Reflux	61	0.95	100 200	6.6 14.5	2.6 5.7	Benzene-ethylene dichloride
Stedman 104	29	Total Reflux	61	1.9	150 500 900	6.8 46.9 61.0	2.7 18.5 24.0	Benzene-ethylene dichloride
Stedman 112	29		61	2.5	150 500	4.8 35.8	1.8 14.1	Benzene-ethylene dichloride
Spiral Screen	30	Total Reflux	43	1.9	900 100 300 500 700	38.1 1.7 1.7 1.76 2.26	15.0 0.67 0.67 0.68 0.90	Benzene-ethylene dichloride n-heptane-methyl cyclohexane
			43	1.3	100 300 400	1.7 1.7 1.87	0.67 0.67 0.74	

valve in the stillhead. Liquid or vapor is intermittently removed as the distillate product.

3. The use of a constant reflux ratio distilling head (Corad head).

The manual control of the reflux ratio is very tedious and unless low reflux ratios are used, it is impossible to estimate them. There is, however, a definite advantage in using manual control, especially in laboratories where other facilities are not available. A common type of stillhead in which the reflux ratio is regulated with a stopcock is shown on the fractionating column in Fig. 205. The two drop counters, one in the product line and the other in the liquid reflux line, can be used for setting the reflux. A second stillhead for manual control is shown on the column in Fig. 206. A third stillhead arrangement is shown in Fig.



191A. This head is recommended when fractionations are performed at reduced pressure. Condensation of vapors of high boiling materials need not take place in the water-cooled condenser which is attached to the top side arm. All condensate outside of the vacuum jacket is returned to the small cup. The reflux is adjusted with a stopcock according to the drops which leave the glass alembic and product drop counters. It is sometimes convenient to slot the plug of the stopcock so the smaller flows can be ob-

tained. This is accomplished by filling a small groove on opposite sides of the bore opening with a three-cornered file. These slots should be $\frac{1}{16}$ " long.

A fourth method of manual adjustment of the reflux ratio was recommended by F. D. Rossini.³¹ A portion of the head is illustrated in Fig. 191B. The glass plug can be raised or lowered by a hand screw which has small threads. This handscrew is held in place by a housing which can be made leak proof by using a bellows.³¹ The glass plug is sealed to a tungsten rod. The arrangement of obtaining the reflux ratio is by counting the drops at the reflux and product drop counters.

The effect of constant versus intermittent product withdrawal from fractionating columns has not been extensively studied. It has been assumed that constant removal of

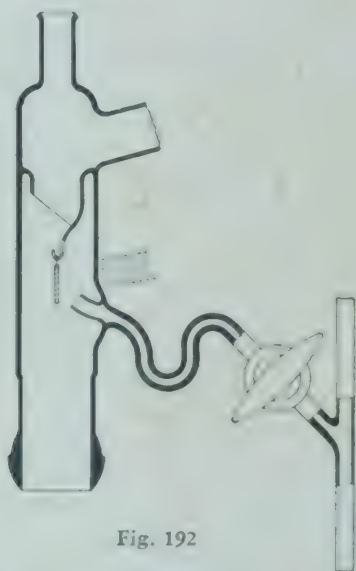


Fig. 192

product was the best way to operate columns. D. M. Oldroyd and L. A. Goldblatt³² have shown that when efficient packing is used (Podbielniak Heli-Grid packing) more efficient separation can be expected with intermittent product removal. Less efficient packing as $\frac{3}{16}$ " Fenske-type glass helices and a Palkin type gauze plate column did not show such a pronounced advantage as the Heli-Grid packing. If efficient packing is available, it is desirable to use stillheads which permit intermittent product removal. Stillheads which can be operated at intermittent take off require solenoid valve arrangements. The following discussion will cover a few such stillheads.

The stillhead of the Podbielniak Hyper-Cal fractionating column is shown in the column assembly in Fig. 203. As

Inconel ball seats in a ground glass recess. This ball is attached to a magnetic armature by a hollow Inconel tube which has a vent at the top. A solenoid coil is located above the dual U-tube condenser. The drippers on the condenser tip are so arranged that the condensate is directed on the Inconel stem and ball. The valve is operated by a cycle timer. Valve travel can be adjusted by the screw above the solenoid coil. The entire condenser is housed in the vacuum jacket. The void space between the top of the Heli-Grid packing and the tips of the condenser is quite small. The hold-up of the head is small. The vapor temperature is determined by a thermocouple.

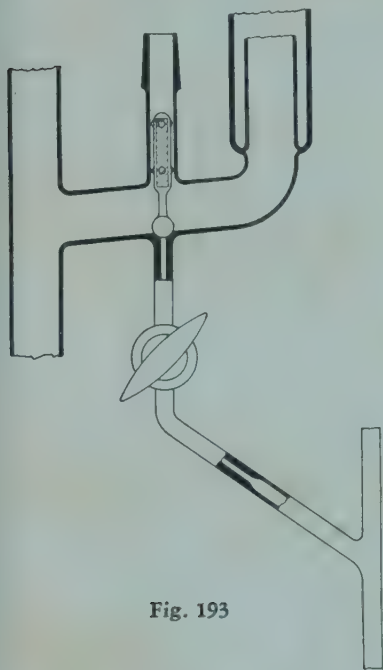


Fig. 193

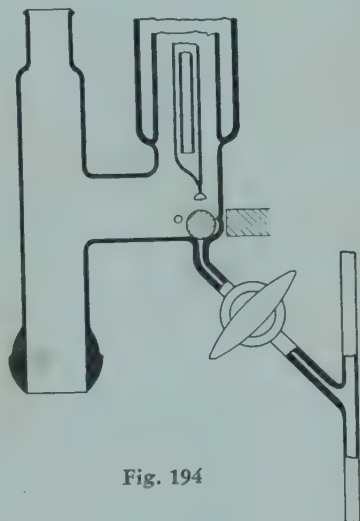


Fig. 194

The stillhead similar to the one shown in Fig. 193 was used by E. A. Naragon and C. J. Lewis³³ on a vacuum column. The solenoid coil is placed over the center tube containing the glass valve. The ground joint facilitates removing the movable glass valve and cleaning of the valve seat. This joint is covered with the cap of the second member of the joint after the solenoid coil is in place. The stopcock need not be used while the column is in operation.

The stillhead in Fig. 194 contains a steel ball which is lifted slightly when the iron core is magnetized. This steel ball is held in place by two indentations on both sides of the reflux tube. These indentations are shown as small rings to the left of the ball. The finger condenser in this assembly has a drop counter.

The stillhead which is illustrated on the continuous fractionating column, Fig. 208, is another example of a glass solenoid valve. All reflux from the total condenser flows through the valve back into the column. Part or all of this liquid stream is diverted to the distillate product receiver when the solenoid coil lifts the glass covered iron core. This arrangement of outside return line and take off valve has



Fig. 195

the disadvantage of having a greater hold-up than is obtained in the stillheads described above. In continuous fractionation this hold-up is not too serious because the reflux is of a constant composition.

The vapor dividing stillhead described by F. C. Collins and V. Lantz⁷ operates on the solenoid ball valve principle. The vapor from the column is directed either into a Dewar-jacketed total reflux condenser or to the product condenser. The glass ball is lifted by a solenoid coil. The temperature is obtained by a partial-immersion thermometer. The still-head is Dewar-jacketed. The reflux condenser and ball of the valve can be removed because the standard taper assembly fits into the joint in the stillhead.

J. D. Bartleson, A. L. Conrad and P. S. Fay³⁴ have described a stillhead with the valve arrangement consisting of a glass covered steel ball in a funnel. This funnel containing the ground surface is located directly under a liquid directing funnel and below the total condenser. Product is removed by magnetizing an iron core in a solenoid coil. The ball is drawn partly out of the funnel allowing liquid to flow into a product receiver.

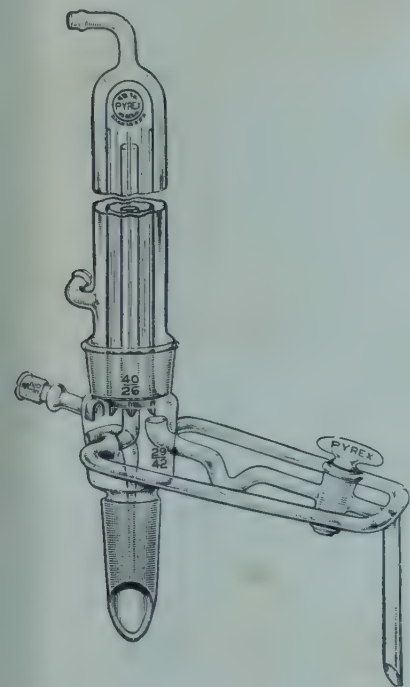


Fig. 196

The solenoid operated valves described above must be clean. Probably the greatest fault of these valves is the fact that liquid will leak through them if the surfaces are not perfectly ground and clean.

Another type of stillhead which is operated by a cycle timer is shown in Fig. 192. H. J. Hepp and D. E. Smith³⁵ have used this stillhead on a precision fractionating column.

This type of head differs from the ball valve heads in that the reflux liquid is directed to the product cup. A solenoid coil around an iron core is used to swing the iron wire against the one wall of the product receiver cup. Reflux then drains into this cup through the U-tube vapor seal and into the product receiver. When the iron core is demagnetized, the iron wire is swung back into a vertical position by gravity. A vapor line from the top of the total condenser (not shown in Fig. 192) is connected to the product outlet line. The stopcock shown in the product line is not used during operation. It is helpful when the distillation is first started.



Fig. 197

The stillhead developed by A. S. Carter and F. W. Johnson³⁶ is shown in Fig. 195. This liquid-dividing head is manufactured and sold by Ace Glass, Inc. This stillhead contains a swinging funnel to which is attached a glass-covered iron core. The funnel is drawn over a product receiver cup when an iron core is magnetized with an electromagnet coil and swings back into normal position when the iron core is demagnetized. When the funnel is in its normal position, reflux drains from a funnel just below the total condenser into the swinging funnel and into the third fixed funnel which is centered in the vapor tube from the column. The temperature is obtained by a partial immersion thermometer which is located in the ascending vapor line.

A stillhead with a swinging funnel has also been developed in the Shell Development Laboratories and described by F. C. Collins and V. Lantz.⁷ The stillhead has a Dewar-jacketed total condenser which fits into the ground joint of the Dewar-jacketed liquid-dividing stillhead. This stillhead has a vapor tube leading to the condenser, a liquid return line to the column and a liquid product line which contains a vapor seal in the form of a U-tube.

Constant-ratio Stillheads

The constant-ratio head is a recent innovation in fractionating column stillheads. The design and application of such heads is discussed by L. Berg³⁷ and by L. E. Lloyd and H. G. Hornbacker.³⁸ These heads are called Corad heads—COnstant-RATio head. These stillheads operate on the principle of two parallel condensing surfaces, one for product and the other surface for reflux. The Corad head developed by L. E. Lloyd and H. G. Hornbacker is shown in Fig. 196. This head is manufactured and sold by the Corning Glass Works. The head is fabricated for approximate reflux ratios of 1.5:1, 2.5:1, 5:1, 10:1, 20:1 and 30:1. The different ratios are obtained by turning the condenser which has drippers for each condensing area over the product receiving cup. The stillhead designed by L. Berg is shown in Fig. 197.

The advantages gained by using the Corad head are obvious. The reflux is dependent on condensing area exposed to the vapors. A change in boil-up rate in the column will effect the take-off rate in the same ratio as before. Consequently, changes in boil-up rates during a distillation are not too serious. Distillation of liquid which yield a condensate of two liquid phases also does not hinder the operation. One disadvantage which may be cited is that high reflux ratios (100:1) cannot be obtained without greatly increasing the area of the condensing surface.

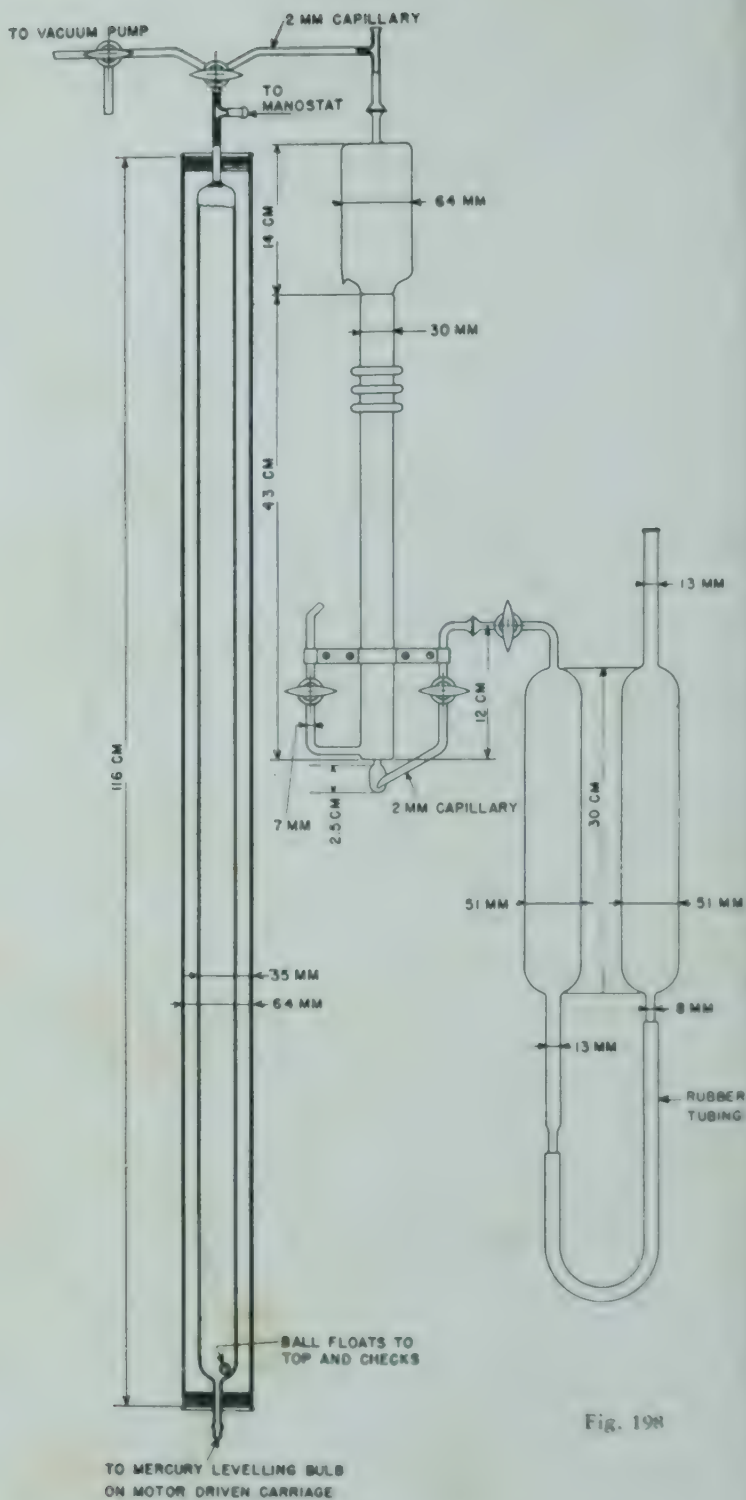


Fig. 198

FRACTIONATING COLUMNS FOR HYDROCARBON GASES

Fractionating columns for hydrocarbon gases have been developed as a laboratory tool for the analysis of gases. Such columns have been used with a great deal of success in the petroleum industry. The identification of gases obtained in various processes has been of greater value to this industry than purification of gases in small scale fractionating columns. Consequently, discussion of the construction of small fractionating columns will be devoted to equipment with which suitable analysis can be made.

A semi-automatic low temperature fractionating apparatus for the identification of hydrocarbon gases was developed in this laboratory. Several requirements were set up before the column and auxiliary equipment was designed and constructed. It was desirable to have a distillation apparatus which would give good results with gas sample volumes of 150 to 500 cc. These small samples made it necessary to have a column with a small hold-up as well as sufficient fractionation to identify various components in the gas mixtures. Semi-automatic operation was desired as the recording of distillation curves.

The assembly of the glass parts of this small fractionating apparatus is shown in Fig. 198. The various parts of the assembly will be described in the following discussion.

The Stillpot and Vapor Pump

The stillpot has a volume of about 3 cc. A glass vapor tube, 2 mm. bore capillary, is sealed into the side of the stillpot. The other end of this glass vapor tube is later sealed to a gas manifold containing two stopcocks and a mercury pump in respective order. Dimensions for the manifold and pump containers are given in Fig. 198.

The Column

The column is made from a 60-cm. length glass tube with an internal diameter of 2.5 to 3mm. The bore of this tubing should be uniform. This tube is packed with a 45-cm. length of spiral made from No. 24 B&S copper wire. The spiral is wound to give two turns per centimeter length. A tapered

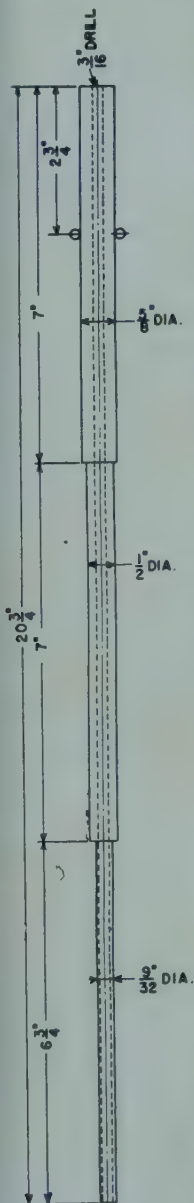


Fig. 199

jacket is machined from a copper rod. The form and dimensions of this jacket are shown in Fig. 199. A copper ring is soldered to the tapered jacket. A silvered glass jacket containing three outside expansion bellows and a side tube for periodic evacuations of the glass jacket is made as shown in the assembly in Fig. 198. The inside tube of this jacket has a diameter of 18 mm. The construction of the condenser flask has been previously discussed and illustrated in Fig. 143, A and B.

The column is assembled by inserting the small-diameter end of the copper jacket into the top of the condenser Dewar. This Dewar is moved into position under the copper ring near the top of the copper jacket. Several layers of adhesive tape can be used at this point to insure a seal between the Dewar and copper jacket. The silvered glass jacket is then slipped over the copper jacket and the annular space is filled with ground cork. The column is then slipped into the copper jacket. A spherical ground glass joint is sealed to the column about 2 cm. above the Dewar condenser.

A two-junction copper-constantan thermocouple is inserted through the top of the vapor line tee to a distance 2 cm. above the top of the spiral packing. The thermocouple wires are sealed into the one tube of the tee with DeKhotinsky cement.

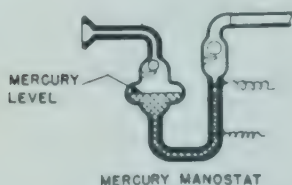


Fig. 200

The Vapor Manifold and Product Receiver

The vapor manifold must have as small a volume as possible. Two-millimeter bore capillary tubing is used. The manifold extends from the column through three-way stopcocks. The outlets of the first stopcock are sealed to the vapor line from the column, the product receiver line and to the one outlet of second stopcock. The remaining outlets of the second stopcock serve as lines to the vacuum pump and a drying and purifying train respectively. The pressure manometer is teed into the line going to the product receiver. This manometer must be cleaned periodically and consequently is best connected to the vapor manifold through a spherical glass joint. The pressure manometer is shown in Fig. 200. This manometer has two platinum contact points sealed into the glass. A small level change in the large leg which is connected to the vapor line causes a correspondingly larger change on the narrow contact leg. The manometer has two check balls which prevent the mercury from leaving the manometer.

The product receiver is about 100 cm. long and 25 mm. in diameter. It is jacketed with a section of 64 mm. tubing. This jacket serves as a constant-temperature bath. Water from a thermostated bath is pumped through the jacket

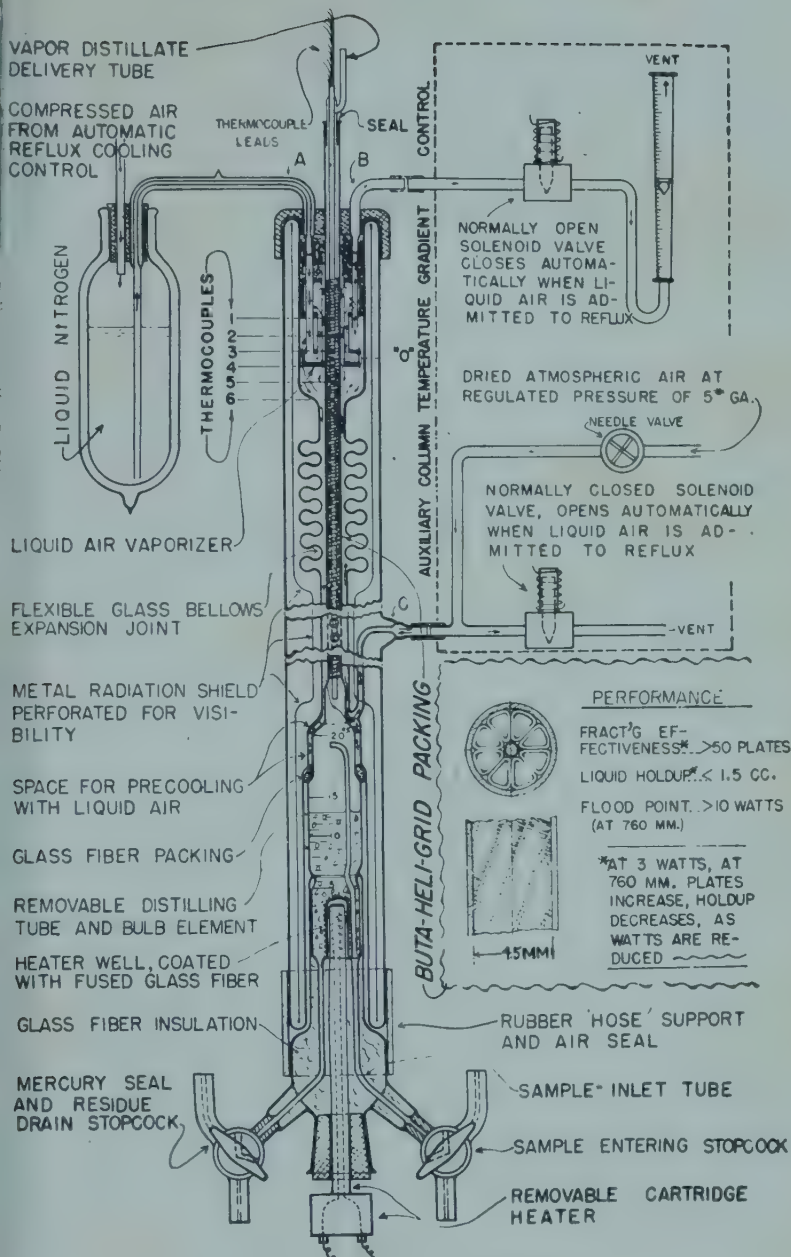


Fig. 201 (Drawing courtesy Podbielniak Inc.)

Mercury is the confining liquid in the product receiver. A glass ball on the mercury serves as a check which prevents the accidental transfer of mercury into the vapor manifold. The top outlet of the product receiver is ground to insure a good seal with the floating ball. The mercury in the product receiver is raised and lowered by a leveling bulb. This bulb is supported in a holder which is attached to an elevator screw.

Elevator Mechanism

The elevator or leveling device is a long threaded screw and collar. The mercury leveling bulb is attached to the collar. The screw is driven by an a-c. motor through a reduction gear. The motor is braked to prevent coasting after the current is turned off. The motor is connected to the electrical power source through the relay of a United Cinephone electronic switch, Model 8282. When contact is made in the pressure manometer the motor is started.

The mercury is lowered in the product receiver by the turning of the elevator screw until normal pressure is established in the vapor manifold. The elevator screw is connected directly to the advancing mechanism of the Leeds & Northrup recording potentiometer through a speedometer cable.

The Operation of the Semi-automatic Fractionating Column

Since the total volume of gas entering the product receiver is a measurement of chart length, it is helpful that two points be marked on the screw carriage. The first or zero point is the mark which gives a mercury level to the top of the product receiver. The second mark is arbitrary. This mark toward the bottom of the screw corresponds to chart travel and should be low enough to utilize the greater portion of the product receiver volume.

The apparatus should first be tested for leaks. The vapor line up to the stopcock nearest the still pot is filled with mercury and the stopcock is closed. The screw collar is set at the second point discussed above and the entire apparatus is evacuated to a pressure of about 1 mm. of mercury. The mercury rises in the product receiver equivalent to the barometric pressure minus the small residual pressure in the apparatus. This level is watched for several minutes after the apparatus is isolated from the pump. A drop of the mercury level in the product receiver indicates a leak.

The sample is introduced through a drying and CO_2 absorbing train into the product receiver. Sample from this receiver is allowed to flow into the vapor line and column by periodically turning the three-way stopcock until the gas in the apparatus is at atmospheric pressure.

The sample is transferred into the first receiver of the mercury pump. The carriage containing the leveling bulb is raised to the zero point mark after the connecting rubber tube is closed with a screw clamp. The stopcock nearest the stillpot is opened as the leveling bulb of the mercury pump is slowly lowered. The flow of gas from the product receiver to the pump reservoir is regulated by the screw clamp and the rate of lowering of the mercury pump leveling bulb. The pressure within the apparatus should not vary appreciably from atmospheric pressure in this operation.

The stillpot is cooled with a Dewar containing liquid nitrogen. Condensable gases in the column and vapor lines are condensed in the stillpot. When condensation is complete the condenser of the column is cooled by pouring liquid nitrogen into the condenser flask. The advancing mechanism of the recorder is connected to the speedometer cable and the power switch to the electronic relay thrown to the on position. The gas sample in the mercury pump reservoir is then slowly transferred to the stillpot. If non-condensable gases are present, as air or hydrogen, the contacts of the pressure manometer are contacted and the motor is started. The product receiver leveling bulb is lowered until the pressure in the apparatus is again restored to atmospheric pressure. The temperature is recorded on a chart during the lowering of the leveling bulb. When all the gas has been transferred to the stillpot and column, the condenser is maintained at liquid nitrogen temperature and the distillation is started by removing the liquid nitrogen Dewar from the stillpot. Usually sufficient boiling can be obtained by allowing the stillpot to warm slowly. A chilled empty Dewar around the stillpot will prevent air drafts and also allow sufficient boiling. The condenser is kept cold and a temperature gradient is set up between this point and the stillpot because of the tapered copper column jacket. As the distillation progresses, the chart shows definite plateaus for each component which can be separated by the column packing used. The distillation continues until the collar indicator reaches the end point mark.

Two corrections must be applied before the chart is complete. In all distillations, the gas must fill the lines beyond the thermocouple before the pressure manometer is activated. This correction can be made if the volume of this section is known as well as the total volume of the sample. This correction usually amounts to not more than 3 mm. of chart length and is added to the length of the first temperature plateau. The last temperature plateau of the distillation is short by the volume remaining below the thermocouple. This volume can easily be determined. The plateau length corresponding to this correction usually is about 8 mm. and is added to the final plateau if there is no material in the stillpot which cannot be vaporized at room temperature and atmospheric pressure.

Binary mixtures of iso- and n-butane (which boil within $10^{\circ}\text{C}.$) exhibit a slight discrepancy in values observed, to the values actually present. It is possible to check synthetic blends and to draw up calibration curves which can be used for correcting the observed values.

The analysis of gas samples containing olefins requires two distillations. A sample for complete analysis of olefins and paraffins is distilled in the apparatus by the procedure outlined above. The total sample is brominated noting the contraction in volume. The gas remaining after the bromina-

tion is distilled. Results of the second distillation when multiplied by the contraction factor represent the paraffin content of each fraction in the original sample.

The Podbielniak Low-temperature Fractionation Equipment

A discussion of the low-temperature fractionation of hydrocarbon gases is not complete unless the extensive work of Podbielniak^{5, 22} is mentioned. The low-temperature fractionation equipment which is available from Podbielniak, Inc., Chicago, Illinois is used in many laboratories. The "Heli-Grid" packing and a modification of this packing, the "Buta-Heli-Grid" packing, have been successfully used to obtain satisfactory separations for the analysis of gases.

The basic fractionating element of the Podbielniak apparatus, the "Super-Cool" column, is shown in Fig. 201. This apparatus with the multiple thermocouples along with a special "Buta-Heli-Grid" packing shown in the drawing is used in the "Heli-Tronic" fractionating apparatus for the analysis of C_4 and C_5 hydrocarbons. The columns shown in the "Hyd-Robot" apparatus, Fig. 202, are basically the same except that Heli-Grid packing is used along with a single junction thermocouple.

The "Super-Cool" column consists of a vacuum sleeve-type jacket with a sheet metal radiation shield. Enlargements at the top and bottom of the sleeve accommodate the stillpot and the special liquid nitrogen vaporizer and reflux cooler assembly. Liquid nitrogen vapors from the vaporizer pass downward through the annular space between the column and jacket to a point just above the stillpot and out through a glass vent tube to the outlet tube C. The sensible heat of the cold vapors from the reflux cooler is conserved by this arrangement as well as the neutralization of heat leakage through the vacuum jacket. The entire column can also be pre-cooled to liquid nitrogen temperatures in a short time by the cold vapors from the reflux cooler and the direct introduction of this refrigerant through the outlet at C before the gas sample is charged to the stillpot.

Dried air can be automatically introduced through the needle valve in a line leading to the side opening C. This dried air passes up through the annular space around the column giving a period of super-heating. This warms the entire column very rapidly at breaks, i.e., raising temperature to distilling temperature of next higher boiling component. The column can thus be super-cooled by the flow of cold vapors from the reflux head and super-heated with the flow of dried air.

The stillpot is designed so that samples can easily be introduced. Liquid residues can be withdrawn. Heat is supplied to the stillpot by a removable cartridge heater which extends into a heater well. The inner surface of the well is coated with fused glass fiber to facilitate boiling.

The "Hyd-robot" fully automatic distillation apparatus, Fig. 202, contains the following:

1. Two columns with stopcock manifold panel.
2. Automatic recording panel.
3. Multiple distillate receiver tank with five or six equi-volume one gallon bottles which are connected to the stopcock panel. The receiver tank can be supplied with an automatic constant temperature control.
4. Mercury pump panel.
5. Fraction collecting burette panel.
6. Auxiliary equipment as a vacuum pump, liquid air container apparatus for column operation.

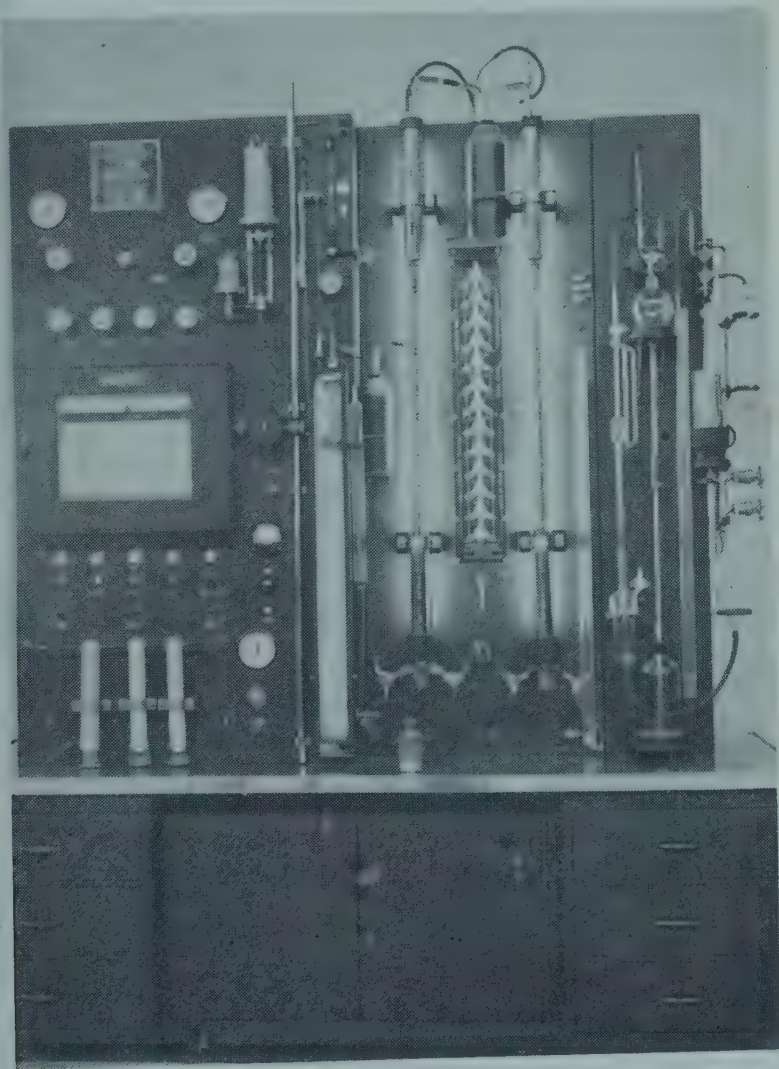


Fig. 202

Numerous other fractionating assemblies can be supplied to meet the demands of the laboratory.

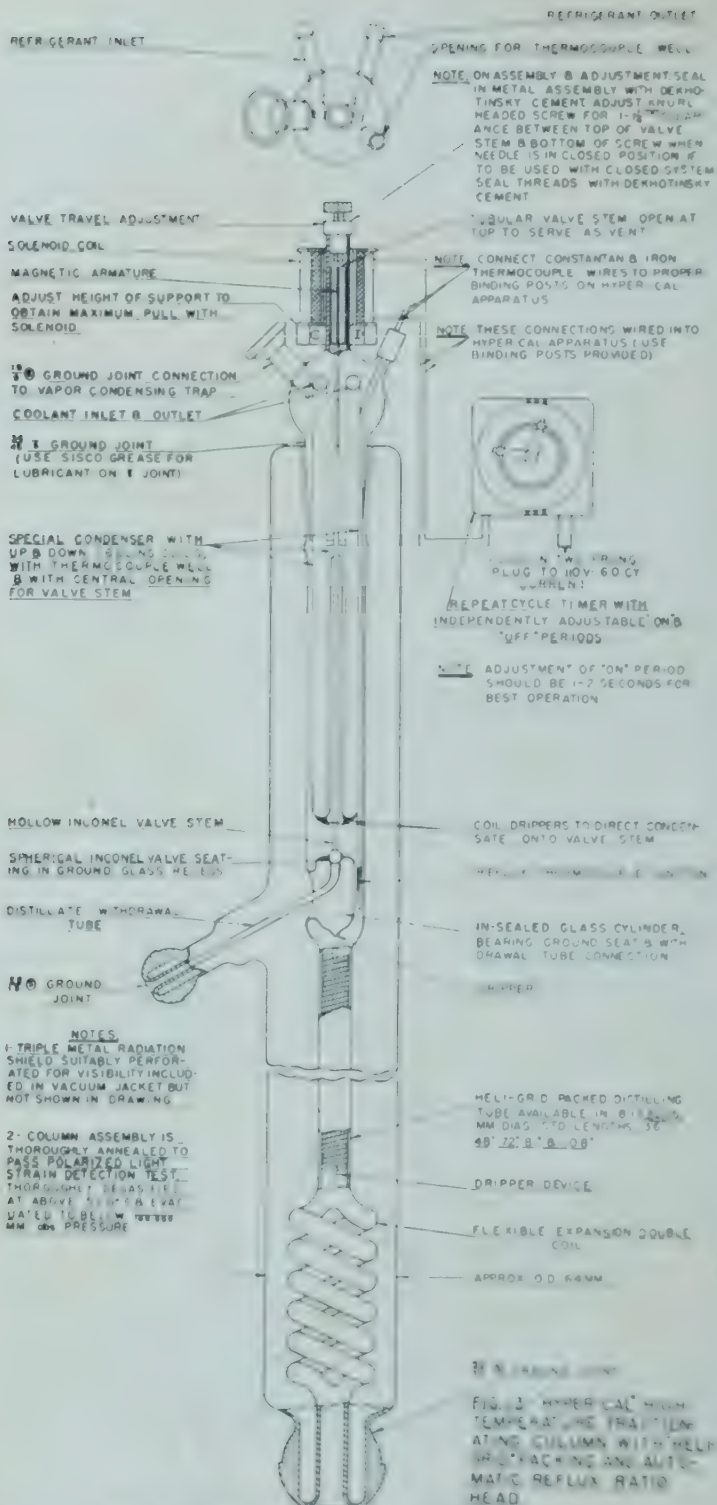


Fig. 203 (Drawing courtesy Podbielniak, Inc.)

Recent Developments in Hydrocarbon Analysis

Two important factors must be considered in the method of gas analysis, i.e., the manpower required and time consumed in the analysis. The recent trend in equipment design has been toward semi- or automatic fractionation equipment. The "Hyd-Robot" of Podbielniak, Inc., is a good example of the development of automatic distilling equipment. The time element is one factor which has received attention but unfortunately cannot be solved as easily as the design of automatic equipment. The fractionation process is inherently a slow process and, if extremely rapid fractionations are performed, small samples and extremely efficient packing must be used. Even under such conditions, analytical procedures also must be performed before the analysis is complete, i.e., when olefins are present in the gas samples. The development of infrared spectrophotometry and the mass spectrometer have aided greatly in decreasing the time required for gas analysis. New and advanced techniques have been developed which have made possible very rapid control analysis. It is beyond the scope of this work to discuss the techniques and equipment used in infrared spectrophotometry and the mass spectrometer. It will suffice to mention that fractionation of gas sample into fractions and analysis of the more complex fractions by infrared spectrophotometry is being used in many laboratories.

DISTILLATION COLUMNS FOR THE FRACTIONATION OF NORMALLY LIQUID HYDROCARBONS

The development of laboratory columns for the fractionation of liquid mixtures boiling in the range of 25 to 250°C. has been very extensive. Design problems for this class of fractionating columns are quite simple. Columns can be designed to accommodate specific types of packing which can be used to meet the requirements of many different distillation problems.

The distillation problem should be reviewed before the fractionating column is designed and constructed. The facilities available (manpower and electrical power sources), the amounts of charge to be fractionated and the degree of fractionation required are factors which have a direct bearing on the design and packing used in the column. The column should be so designed to permit a vapor velocity of 1 meter a second. In view of the previous discussion of the individual parts of a fractionating column, it will not be necessary to discuss the column assembly except to give examples of several columns which have been used.

The Podbielniak "Hyper-Cal" Column

The Podbielniak Hyper-Cal column²² is shown in Fig. 203. The condenser is a double loop of glass tubing with drippers

at the bottom tip of the loop. These drippers direct the reflux into the valve stem. A glass cylinder between the condenser and packing decreases the vapor space. This cylinder contains the valve seat and a reflux dripper. The reflux thermocouple junction is located beside this cylinder. Product removal is controlled by a solenoid valve which is operated by a repeat cycle timer with adjustable "on" and "off"

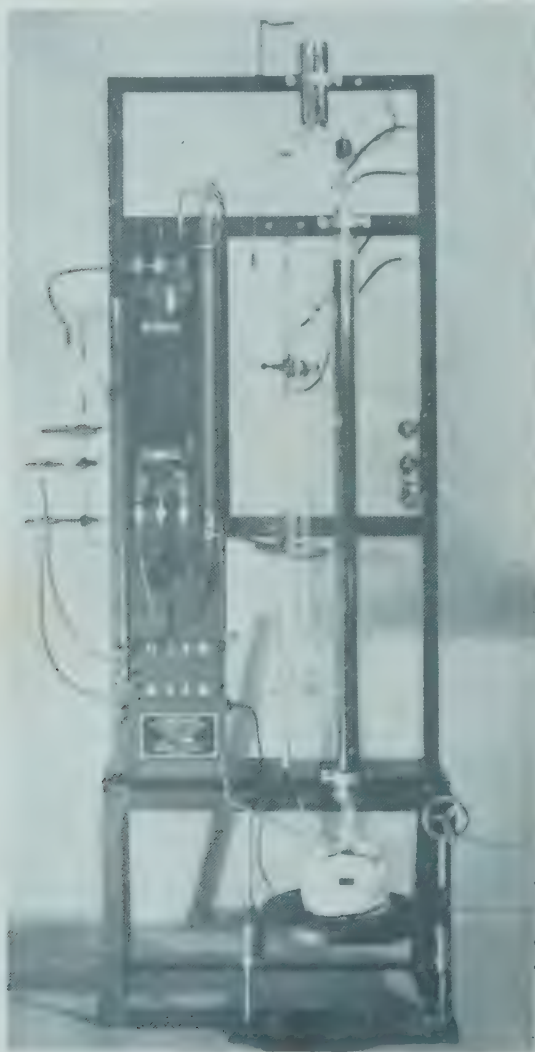
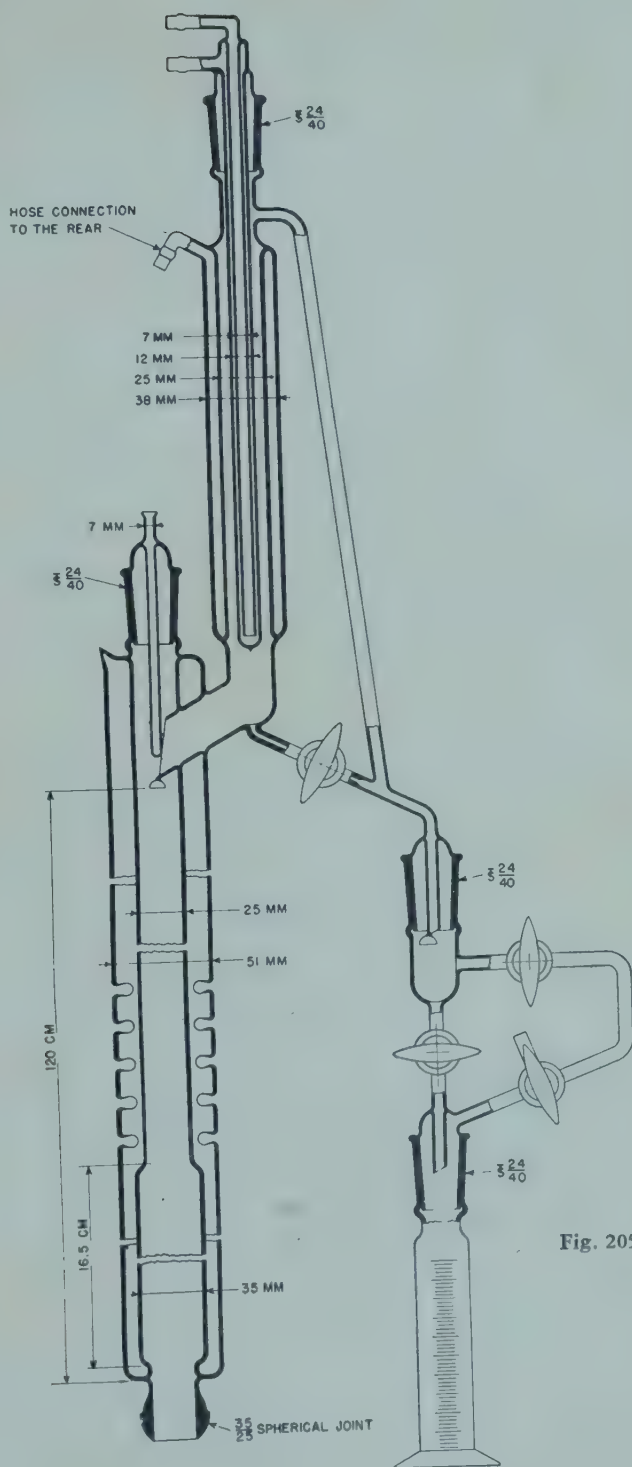


Fig. 204

periods. Product receivers are connected to the column through a 28 15 spherical ground glass joint. The expansion of the column is compensated with a double expansion coil at the bottom of the column. The assembly of the Hyper-Cal column which is available from Podbielniak, Inc. is shown in Fig. 204. An automatic distillation unit containing a



Podbielniak Super-Cal, Model B, distillation unit is described by L. Steffens and D. P. Heath.³⁹

Laboratory Fractionating Column for Manual Control

The vacuum jacketed column shown in Fig. 205 is designed for manual control of the reflux. This column can be fitted with any of the other stillheads that have been previously discussed. The vacuum jacket is silvered to the reflux drop counter or strip silvered. The inside bellows allow expansion of the tube containing the packing. The short section of the column at the bottom which has a larger diameter is used as a knock-down section for high boiling components. Dump-in packing is supported by using a wire gauze cone which can be forced into the spherical joint opening. Tension of the deformed cone is released when the cone is pushed into the larger bore tubing. The apex of the cone should point toward the top of the column while the base of the cone rests on the shoulder formed by the seal between the large and small tube.

Another column which is designed for manual control of reflux is shown in Fig. 206. No jacket is shown around the column. The choice of insulation may be as shown in Fig. 190A or 190C. This column as shown is designed for the dump-in types of packings. The small enlargement near the bottom of the column is for the packing support.

Small-residue Fractionating Column

If a survey is made of the various column packings, it will be noted that each has a certain operating hold-up which make it impossible to make a complete fractionation analysis of the mixtures charged to the column. Smaller columns could be used by sacrificing throughput. The second expedient is to use a smaller column for the fractionation of the residue. A column designed for the fractionation of residues is shown in Fig. 207. The packing should naturally be of the type with a small hold-up. A glass spiral, 6 turns per inch of 3-mm. rod, which fits into the column after it is wound on a glass rod, has been successfully used.

The reflux ratio is controlled by the stopcock. The column is started by turning the condenser so that reflux flows directly to the packing. Product can be removed by turning the condenser so that reflux is directed into the product removal line. The vapor temperature is obtained by a thermocouple in the well which is ring sealed into the inner member of the ground glass joint.

Continuous Laboratory Fractionating Columns

Small continuous distillation units which contain a stripping and fractionating section are very useful for separating mixtures. These columns can be adapted to the fractionation of products from small scale bench scale units especially if the fore or the last portion of a mixture must

be separated from the remainder of the product. If a portion from the middle of the product is desired, two distillations must be made or two columns must be used. The small continuous columns have certain advantages over batch distillation columns. The columns can be operated as product is being produced, large amounts of a mixture can be fractionated without the use of large and cumbersome still-pots and the results obtained by using continuous columns are comparable to those of batch fractionations.

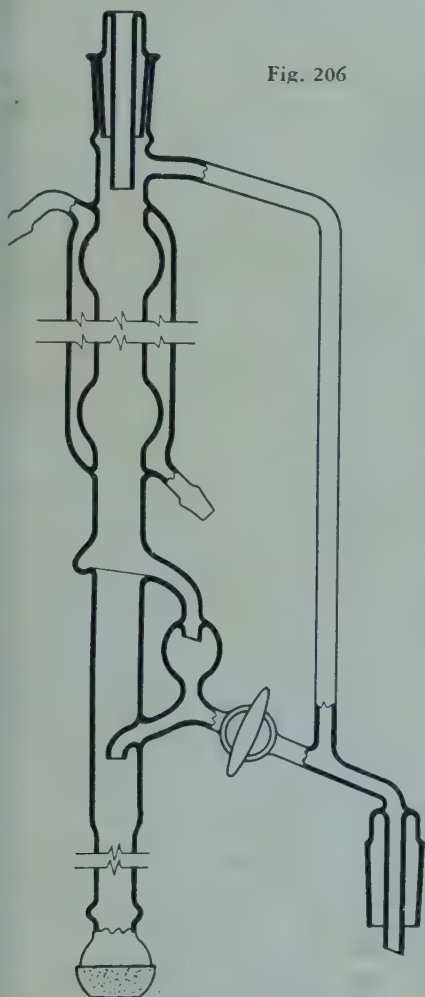
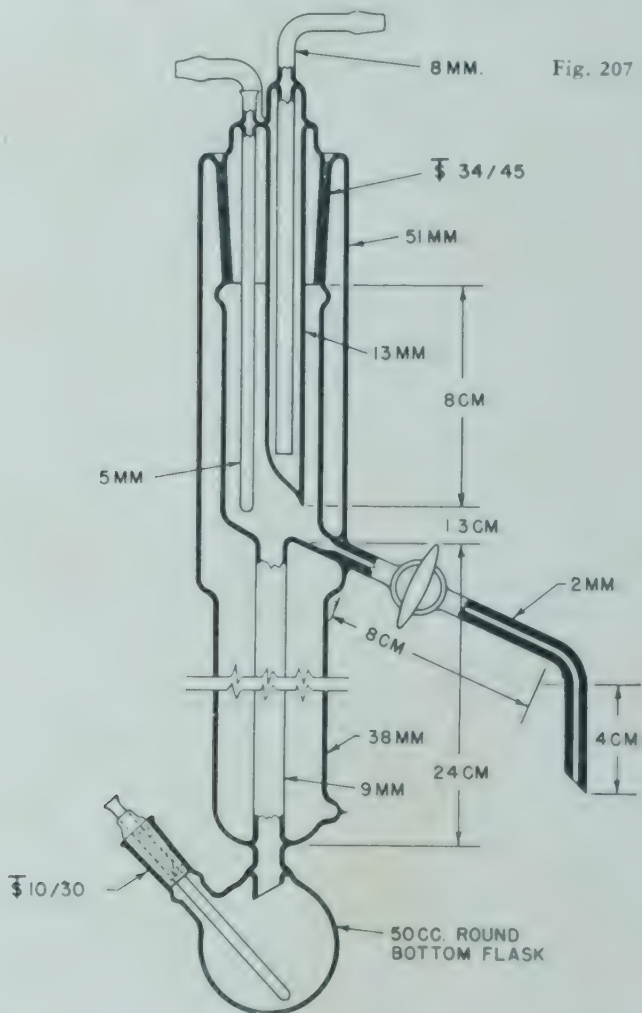


Fig. 206

Very few small continuous distillation columns are reported in the literature. R. W. Hufferd and H. A. Krantz⁴⁰ have described a small continuous metal column along with some tests of fractionating a binary test mixture. The column which has been successfully used in this laboratory is as illustrated in Fig. 208. The charge is pumped into a preheater (not shown) which is connected to the inlet tube in the lower mid section of the column. This preheater consists of a vertical tube 40 cm. long and 18 mm. in diameter. A thermowell which extends the entire length is ring-sealed into the top of the tube. The tube is filled with glass chips. An inlet is sealed to the top of the tube. The preheated charge flows into the column through a tube and spherical joint which is sealed to the bottom of the preheater. Hufferd and Krantz described a preheater which consists of a steel tube coil cast in

aluminum. The preheater is wound with tape and an electrical resistance heater and finally lagged with magnesia pipe covering. The column is insulated as shown in Fig. 190A. At least two electrical resistance heaters are necessary, one for the stripping and a second for the fractionating section.

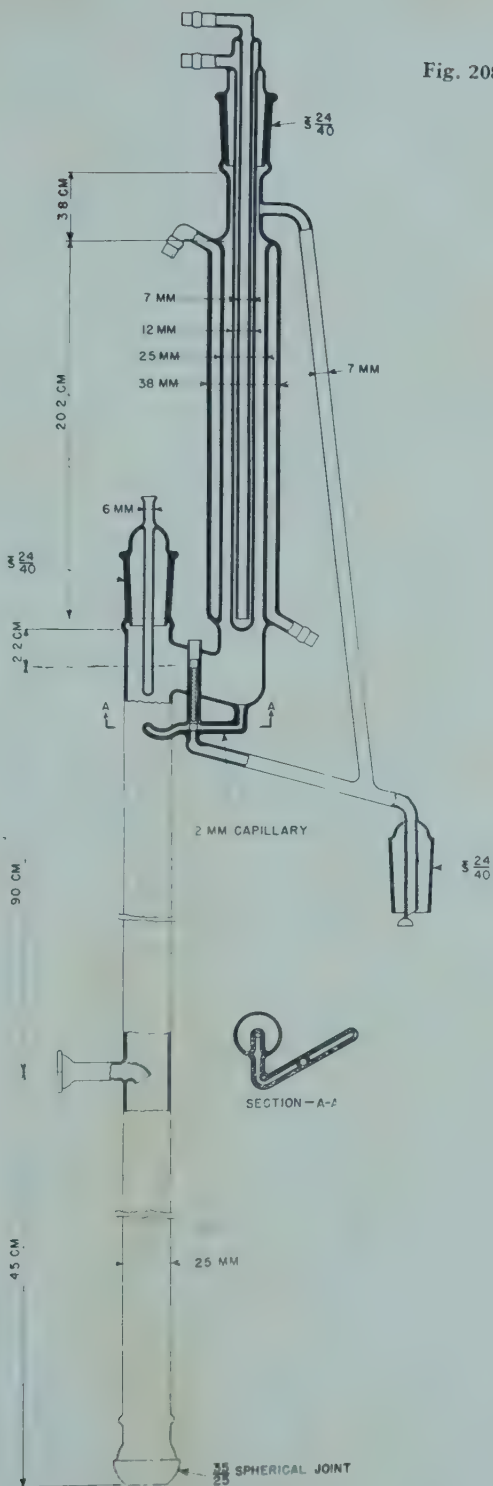
The stillpot (not shown) must contain a thermowell, a sight gage for level indication and a line for the removal of bottoms. The stillpot can be made from a large tube, the size of which depends on the size of the column. A stillpot of 500-cc. capacity is large enough for the column shown in Fig. 208. The sight gage can be sealed at the top shoulder and the bottom outlet tube. An electrical resistance heater, is wound on the stillpot.



The column is fitted with a total reflux condenser. The reflux is returned to the column through a capillary tube which contains a small glass ball solenoid valve. Product is removed during "on" periods of a cycle timer. The adjustable "Flex-o-pulse" cycle timer of the Eagle Signal Corporation is satisfactory.

The column can be operated at a constant overhead temperature because the product has a constant composition. If

Fig. 208



an electrical temperature controller is available, as a Leeds & Northrup "Speedomax" controller, a thermocouple can be used for recording temperatures. This controller can be set at a definite temperature and when this temperature is exceeded, the relay in the controller will shut off the current to the solenoid coil. The column will thus operate at total reflux until the temperature is lowered to the desired overhead temperature. The relay in the controller then closes the circuit to the solenoid coil which opens the valve when the cycle timer moves through the "on" position.

If a temperature controller is not available, a simple mercury thermoregulator can be built into the cap of the ground glass joint which contains the thermowell in Fig. 208. An adjustable contact screw will permit adjustment to the desired overhead temperature. The mercury bulb of the regulator should be located in the vapor stream.

The operation of a small continuous column is not difficult provided a constant pumping rate of the charge is maintained to the preheater. The column will attain the equilibrium conditions possible under the operating conditions. If rapidly changing rates are used this equilibrium is disturbed and poor stripping or fractionation can be expected.

Evaluation of Fractionating Columns

The evaluation of fractionating columns has been described in the literature and will not be given here. C. C. Ward⁴¹ has summarized the methods proposed by M. R. Fenske⁴² and by B. F. Dodge and J. R. Huffman⁴³ and has given sample calculations for the determination of theoretical plates in a fractionation column. Four binary test mixtures which can be used for evaluating columns are also given.

VACUUM FRACTIONATION EQUIPMENT

The design of proper fractionating equipment for vacuum distillation has received little attention by many laboratory technicians. Columns designed for distillations at atmospheric pressure are frequently used under reduced pressure for no other reasons except that good separations were obtained at atmospheric pressure. One has but to make a preliminary calculation of the vapor velocity in the columns under reduced pressure to realize the folly of such an attempt. The conditions which prevail under vacuum require special considerations for column design. It was pointed out that a suitable value of the linear velocity for the design of columns at atmospheric pressure is 1 meter per second. A reduction in pressure from 740 to 7.40 will yield an approximate hundredfold increase in velocity. The linear velocity for vacuum column design should thus be 100 meters a second. One need not then be astonished that atmospheric col-

umns are but poor substitutes as columns for low-vacuum distillations. The vapor velocity is too high in the packed column operating at reduced pressure and no equilibrium between reflux and vapor can be expected. In fact, the liquid reflux can be swept through portions of the packing causing vapor channeling in the other portions. Under the conditions of high vapor velocities in a packed column containing reflux, the pressure drop through the column is high enough that excessive temperatures cannot be avoided in the stillpot.

Considerable interest has recently been displayed in the development of low vacuum fractionating equipment. The design and construction of fractionating columns which can be successfully used in the vacuum range of 5.0 to 0.01 mm. of mercury is not easy because only a very low pressure drop can be tolerated. Another drawback which has hindered the widespread development of low vacuum fractionating columns has been the absence of vapor-liquid equilibria data of binary systems which could be used for testing such columns. F. E. Williams⁴⁴ recently studied the system di-n-butyl phthalate and di-n-butyl azelate at 1 mm. of mercury. Vapor-liquid equilibrium data were obtained at this pressure in a simple equilibrium still. Two vacuum fractionating columns were tested at total reflux with this binary mixture. The first column consisted of a vacuum-jacketed empty tube 180 cm. long and 13 mm. in diameter. The second column consisted of 40-mm. Trubore glass tube, 120 cm. long, fitted with an aluminum spiral made by machining square threads on an aluminum rod. The root diameter of the square thread was 12 mm. and the pitch was two turns per inch. Data of the tests when the pressure at the condenser was 1 mm. of mercury show that the empty tube had from 2.9 to 4.5 theoretical plates at total pressure drops of 1.04 and 3.2 mm. of mercury, respectively. The tests on the spiral column showed 12.6 and 10.8 theoretical plates at respective pressure drops of 0.88 and 4.0 mm. of mercury.

E. S. Perry and R. E. Fuguitt⁴⁵ have studied the vapor-liquid equilibria of two binary systems, di-2-ethylhexyl phthalate-di-2-ethylhexyl sebacate and di-n-octyl phthalate-di-2-ethylhexyl sebacate at 0.1 mm. of mercury. The first binary system has a relative volatility of 2.85 and is recommended for vacuum columns with low efficiencies. The second binary mixture has a relative volatility of 1.21 and consequently can be used for testing efficient vacuum columns.

S. F. Birch, V. Gripp and W. S. Nathan⁴⁶ have described a high-vacuum fractionating column. The column contains an 18 gage stainless steel rotor which is twisted 360°. The column was used in the range of 0.01 to 2.5 mm. of mercury and at stillhead temperatures of 80 to 200°C. A pressure drop of 0.03 mm. of mercury was obtained when the boil-up

rate was 300 cc. per hour. The fractionating power of the column was shown to be greatest at a rotor speed of about 300 r.p.m.

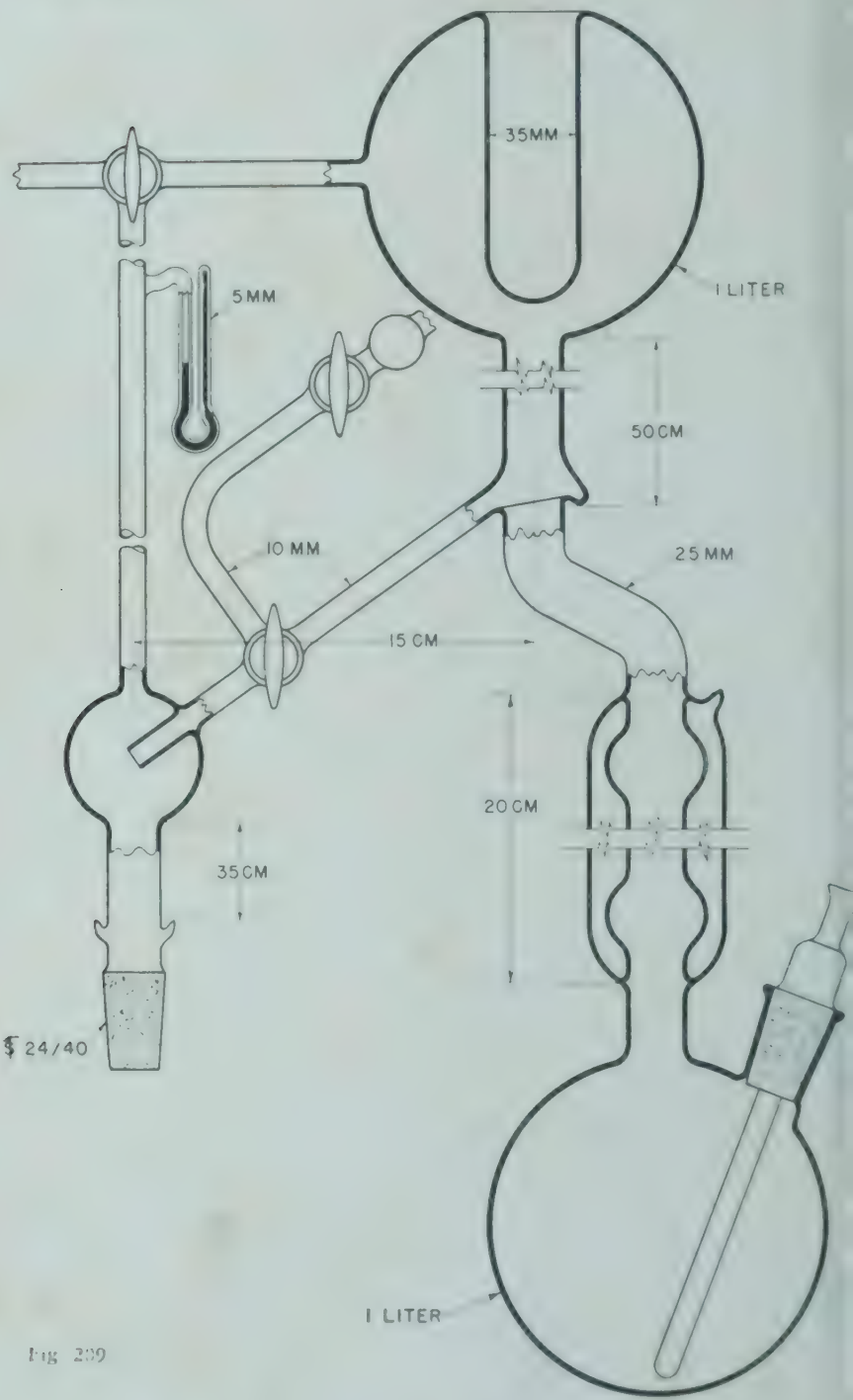


Fig 209

R. Schaffner, J. R. Bowman and J. Coull⁴⁷ have approached the problem of high vacuum fractionation by employing a multiple redistillation principle. The column is a vertical 38 mm. tube, 5 feet long, which contains 12 heated and 12 air cooled zones. The heated zones are 5 cm. long and are wrapped with electrical resistance heaters. Each heated section contains a $\frac{1}{8}$ " Kovar rod spiral with a pitch of $\frac{1}{4}$ ". This spiral which is located inside the column retards the flow of condensate and offers a larger heated surface area. The cooled sections, one of which is located at the top of the column, are cooled with air jets. The partial condenser and stillpot are of a conventional design.

The column operates on the principle of vapor rising in the tube and the countercurrent flow of reflux. Vapors are condensed on the cooled sections and flow to the heated section where they are revaporized. Light components are stripped out of the reflux and the heavy components are returned as reflux. The column has been operated with a test mixture of meta- and para-tricresyl phosphate. The equivalent number of plates of the column were about fifteen.

A useful potstill for low vacuum distillations is shown in Fig. 209. The vapor tube offset acts as a mist trap and successfully prevents liquid carry-over into the product. The vacuum jacketed empty tube offers but little fractionation. The manifold of this still is so arranged that distillate fractions can be removed without breaking the vacuum in still.

MOLECULAR OR SHORT-PATH DISTILLATION

Molecular or short-path distillation has become an important commercial separation process,^{48, 49} the development of which was possible by virtue of its unique characteristics for separating high boiling and heat unstable compounds. The demands of such materials as vitamin A has encouraged the extensive study of methods for performing molecular distillation on a commercial scale. Research on the development and application of laboratory stills has accompanied the commercial development. No attempt will be made to trace the interesting evolution of molecular distillation. The reader is referred to the work of K. C. D. Hickman,⁴⁹ S. B. Detwiler,⁵⁰ C. R. Burch,⁵¹ E. W. Fawcett,⁵² G. Burrows⁵³ and H. I. Waterman.⁵⁴

Molecular distillation may be basically described as a molecular transfer of constituents in a mixture from an evaporating surface to a parallel condensing surface. The residual gas pressure is low enough that the mean free path of the molecules exceeds the distance between the two surfaces. This process of molecular transfer takes place in four steps:⁴⁹

1. The transfer of molecules to the liquid surface.
2. Molecular release at the surface of the liquid.
3. Molecular transfer through the residual gas in the vapor gap between the evaporator and condenser.

4. Condensation.

Equipment design is directly related to these four steps. Since construction of molecular stills will be considered in this section, a discussion of the various basic parts is warranted.

The Evaporator

The essential factor which must be considered in the design of the evaporator is the method of distributing the distillant on the evaporating surface. Quiet surface evaporation is obtained under the low pressure distillation of mixtures containing compounds with high molecular weights. A solution of the evaporation problem as well as preventing excessive decomposition is to spread the distillate over the evaporator in a thin film. Vertical glass and polished chromium-plated nickel has been recommended as suitable evaporator surfaces for falling film molecular stills.

The renewal of the surface of the distillant deserves some comment. F. W. Quackenbush and H. Steenbock⁵⁵ used the expedient of moving rotor composed of three vertical glass rods over the surface of a vertical evaporator. This rotor spreads the liquid over the evaporator and continually exposes constituents below the distillant surface. Glass evaporators with glass rod spirals have been used. A still with spirals will be described later. It should be pointed out that if the spiral fits tight around glass evaporator, some flow of distillant will be obtained along the spiral. Consequently, fairly thick liquid layers will be obtained which favors thermal decomposition.

The introduction of the centrifugal still⁴⁹ by Distillation Products, Inc. illustrates still another method of obtaining a thin film on the evaporator. This evaporator is circular heated rotor with a shallow cone surface. The distillant is fed to the center of the cone. Rotation of the rotor forces the liquid to the outer edges where it is caught by a rotating gutter at the rotor periphery. The residue is collected by a pickup from which it flows to the residue storage flask. The layer of distillant is much thinner on this evaporator than the falling film discussed above. Evaporated materials are collected on a condenser which is located directly in front of the rotor.

The method chosen for heating the evaporator depends on the type of still. Electrical resistance heaters can be used provided the heat can be equally distributed. Small laboratory stills are also heated by boiling certain compounds in a confined heating system.

The Condenser

The condenser does not require special designs except that it should be parallel and near the evaporator. It is no problem to condense the high molecular weight compounds which

are distilled in a molecular still. Water or, more generally, air cooled condensers are adequate.

The Degasser

Any organic liquid which is exposed to the atmosphere dissolves a certain amount of air. When this liquid is subjected to vacuum in the order of 0.001 mm. of mercury and elevated temperature, the air is released and foaming results. Since the space between the evaporator and condenser is small, foaming is to be avoided because of the danger of contaminating the evaporated product. It is, therefore, necessary to have a degassing section in the molecular still. A glass tube wrapped with an electrical resistance heater is quite satisfactory for small laboratory stills. The charge to the molecular still is first pumped through this heater with successive reductions in pressure until the oil is entirely degassed. It can then be pumped to the evaporator.

Vacuum System

The vacuum system will require a good mechanical and a high speed condensation pump. All vacuum lines should be large so that the high speed condensation pump is not throttled. The measurement of pressure within the molecular still requires a gage which does not affect the pressure within the still. K. C. D. Hickman⁴⁹ has chosen the Pirani gage which is periodically calibrated with a McLeod gage. The latter gage is used on the dual molecular still in Fig. 210 and appears to be the choice of numerous small laboratory stills, even though this gage fails to register condensible vapors.

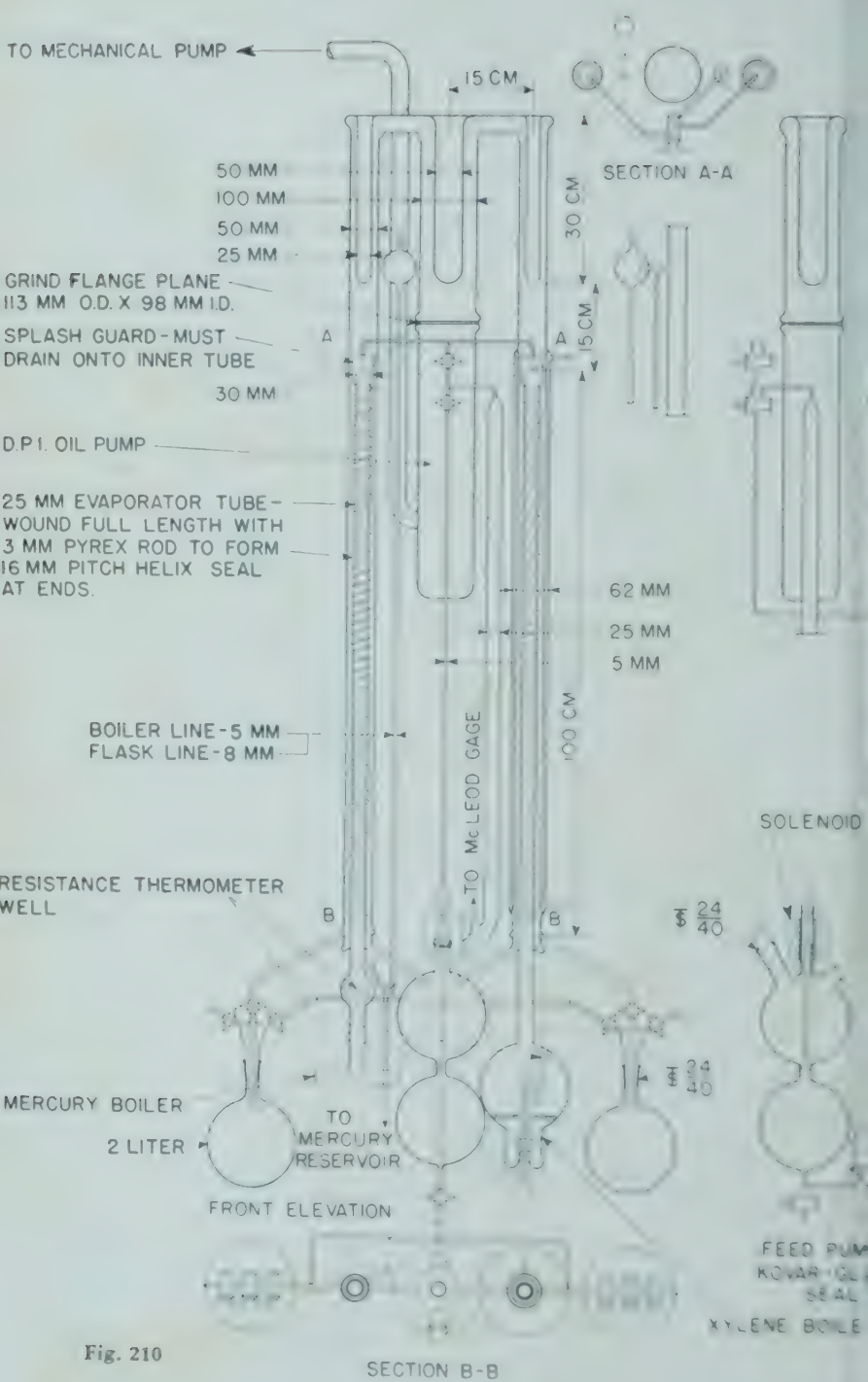
Construction of a Laboratory Molecular Still

A dual falling film molecular still is shown in Fig. 210. This still consists of the following parts:

1. Charge and residue receiver containing two reservoirs connected by a tube. A glass solenoid valve is used to isolate the top receiver from the bottom when residue is being collected during operation.
2. A small gear pump.
3. A tube degasser.
4. A falling film evaporator containing a xylene boiler heater and a water cooled condenser.
5. A falling film evaporator containing a mercury boiler heater and an air cooled condenser.
6. A high speed oil condensation pump. The pump used in this system is the glass-metal oil pump, Type 6M-220 sold by Distillation Products, Inc.

Only a few new construction details have not been described in the preceding chapters. The construction of the two evaporators deserves some comment. The 3 mm. glass rod is wound on the 25 mm. tube in the following manner:

A four-foot section of 25 mm. tubing is wrapped with single layer of 0.015" asbestos tape. The 3-mm. rod is sealed directly to the 25-mm. tube about 6" from one end. The rod



is then wrapped over the asbestos paper by heating the rod and rotating the tube. About one turn per inch is satisfactory. After a sufficient length of spiral is obtained, the rod is again sealed to the evaporator tube. The asbestos paper is removed by soaking it in water and pulling it out from under the spiral.

The xylene boiler contains a coil immersion heater and a resistance thermometer. The four leads are sealed into the glass through a press seal which has been previously described. This boiler is filled with xylene to a level 1" above the immersion heater through the tubulation at the side of the evaporator tube. The xylene is then pumped for a short time to remove dissolved air. It is then frozen by immersing the entire flask in a dry ice bath and the tube and flask are evacuated. The system is then closed by sealing the tubulation.

The mercury boiler consists of a flat metal boiler which is sealed to the glass through a glass-to-Kovar seal. The

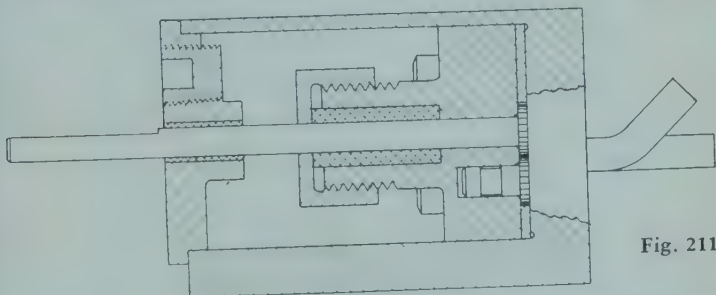


Fig. 211

boiler was previously illustrated in Fig. 83. A ring electrical heater is used to heat the metal boiler. Temperatures of both boilers can be obtained with thermocouples. The mercury boiler also has a temperature indicator which consists of a tube with a small U-tube mercury seal. This tube extends from the glass tube of the mercury boiler to the outlet tube of the condensation pump. The mercury boiler is evacuated through this tube. A line into the U-tube seal from a mercury reservoir below the still is used to seal off the boiler from the vacuum system after the boiler is evacuated. The temperature indicator bar is marked off in temperatures at the heights corresponding to the vapor pressure of mercury.

Both evaporators have splash guards which prevent splashing at the point where the charge enters the still. These guards are spaced to allow the liquid to drain over the evaporator.

Feed Pump

The feed pump shown in Fig. 211 consists of a small gear which can be connected to a variable speed motor and gear box arrangement. Leakage through the pump shaft is prevented by a long stuffing box backed by an oil filled cham-

ber. Kovar tubes which can be soldered to the pump for inlet and outlet lines after glass-to-Kovar seals are made.

Operation of Molecular Still

The operation of a molecular still will depend on the material which is being distilled and the object of the distillation. The degree of separation obtained in a single pass over the

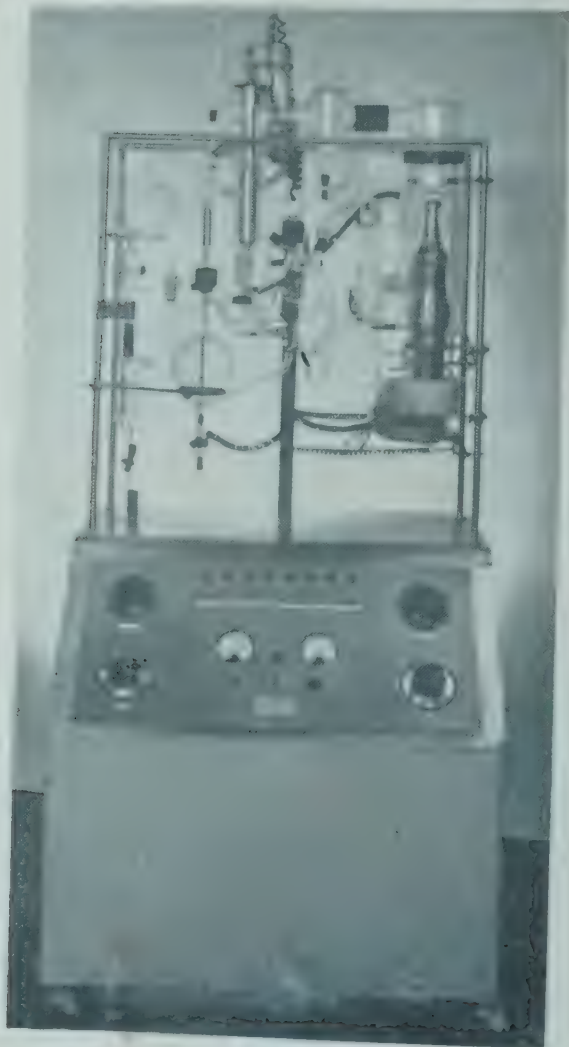


Fig. 212

evaporator is generally less than one theoretical plate. The distillation does not exhibit definite temperatures as obtained in fractionating columns because the residual pressure is very low in the molecular still. Evaporation from the still takes place when a difference of temperature is maintained between the evaporator and condenser. The rate of feed to the evaporator, provided a temperature gradient

between evaporator and condenser is maintained, will also result in different fractions.

Distillation techniques have been developed by K. C. D. Hickman^{49, 56} and N. D. Embree⁵⁷ which are based on the curve obtained by plotting percent yield of a constituent in the various collected fractions against the temperatures of distillation. The circulating batch stills shown in Fig. 210 and 212 can be used for obtaining data for such curves. The mixture is charged to the still and circulated at a constant feed rate while product is removed at a constant evaporator temperature. The temperature is then raised and maintained at this temperature until the second fraction is collected. This process is repeated until all fractions are obtained. If some means is available for analyzing the amount of the constituent in each fraction, it will be noted that a maximum is obtained in the percent yield-temperature curve. Dyes mixed with oils have been used for determining the effectiveness of molecular still. The amount of dye in each fraction is determined colorimetrically.

Hickman⁴⁹ has given a thorough discussion of various applications of the elimination curve techniques. This publication should be carefully studied for information concerning further application of the molecular still.

The operation of a molecular still, Fig. 210, consists of degassing the mixture and then collecting fractions at various evaporator temperatures. The degassing step consists of using a constant temperature in the degasser. The oil is recycled through the degasser as the pressure is lowered in steps as 10, 1, 0.01, 0.001 mm. of mercury. This is accomplished by controlled leaks. When the mixture is degassed and the desired vacuum is reached, the mixture is pumped to the evaporator which is held at a constant temperature. A feed rate of 1.2 liters per hour has been used on the still illustrated in Fig. 210. The fraction is collected at this temperature. The temperature is then raised 10°C. or to any predetermined level and the remaining mixture is cycled over the evaporator and another fraction is collected. This procedure is followed until the maximum recommended temperature of the evaporator is reached. In some instances, some difficulty is experienced due to decomposition at the higher temperatures. Less residence time on the evaporator will help in this situation. The Xylene heated still can be used up to 170°C. The temperature range of the mercury heated still is 150°C to 375°C.

The cyclic molecular falling film still, Type CM5-1000 sold by Distillation Products, Inc. is shown in Fig. 212. Materials which evaporate readily between 100 and 300°C. in a high vacuum (such as organic compounds with molecular weight between 100 and 1000) are fed from a one-liter reservoir by a magnetic circulating pump through a pre-heater tube to

the top of a hot metal column. As the oil flows downward in a thin film over the column, the more volatile fractions distill across to the glass wall and are guided by an alembic to a receiving bottle. The residue drips from the bottom of the column over the bulb of a thermometer and then into a second one liter reservoir. The residue may be cycled as many times as necessary by opening a magnetic ball valve and passing it on to the first reservoir and circulating pump the temperature of the metal column being raised each time to maintain the correct rate of distillation. The still can be used as an analytical device by controlling the increments of column temperature and time of distillation according to the "elimination curve technique" developed by K. C. D. Hickman^{49, 56} and N. D. Embree.⁵⁷

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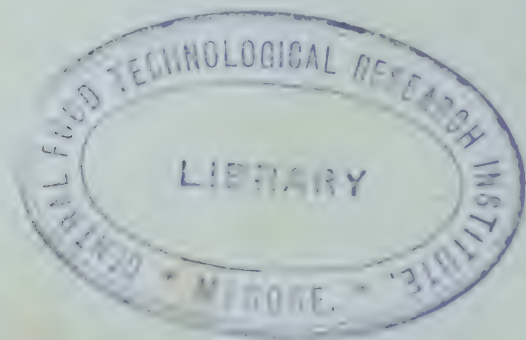
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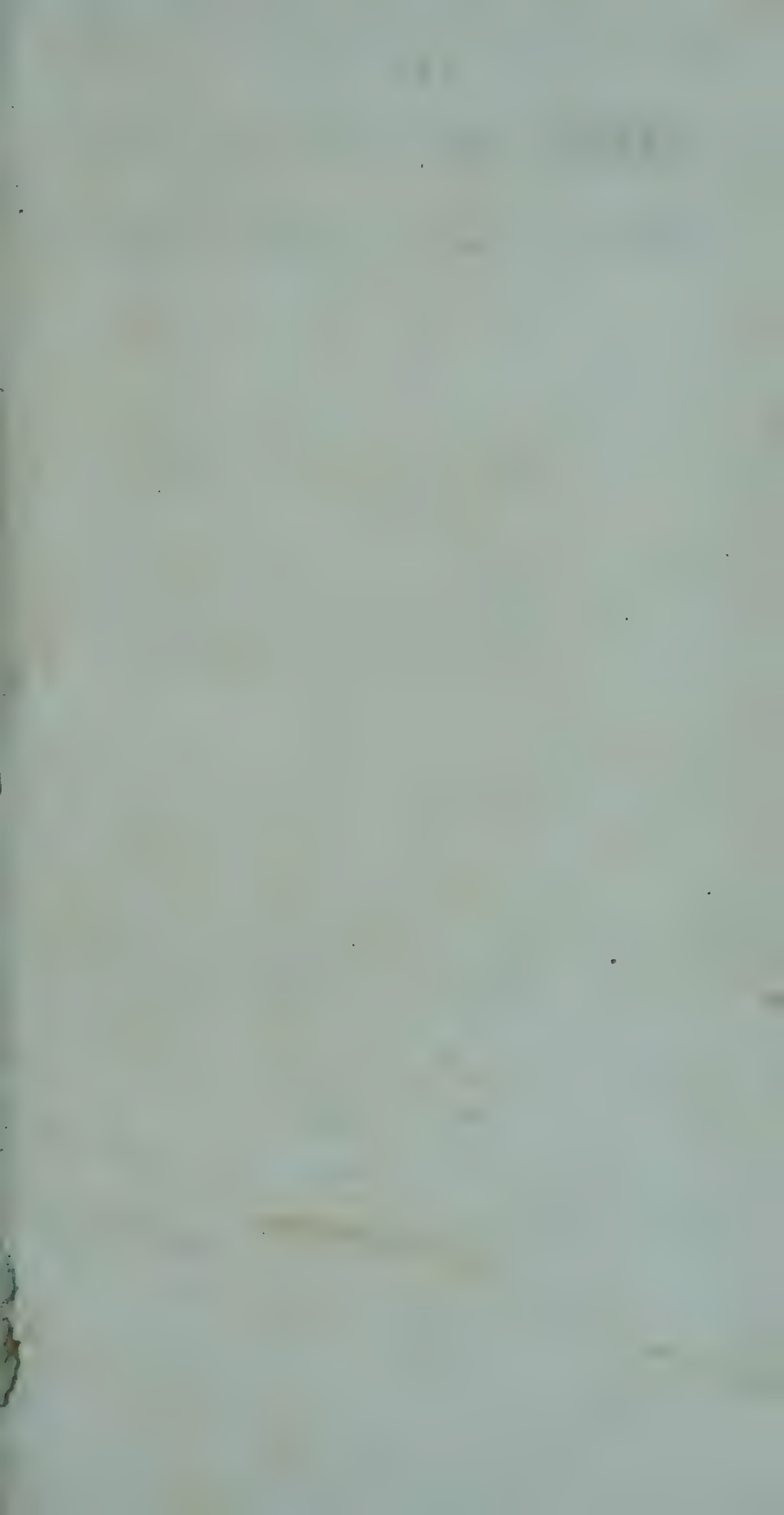
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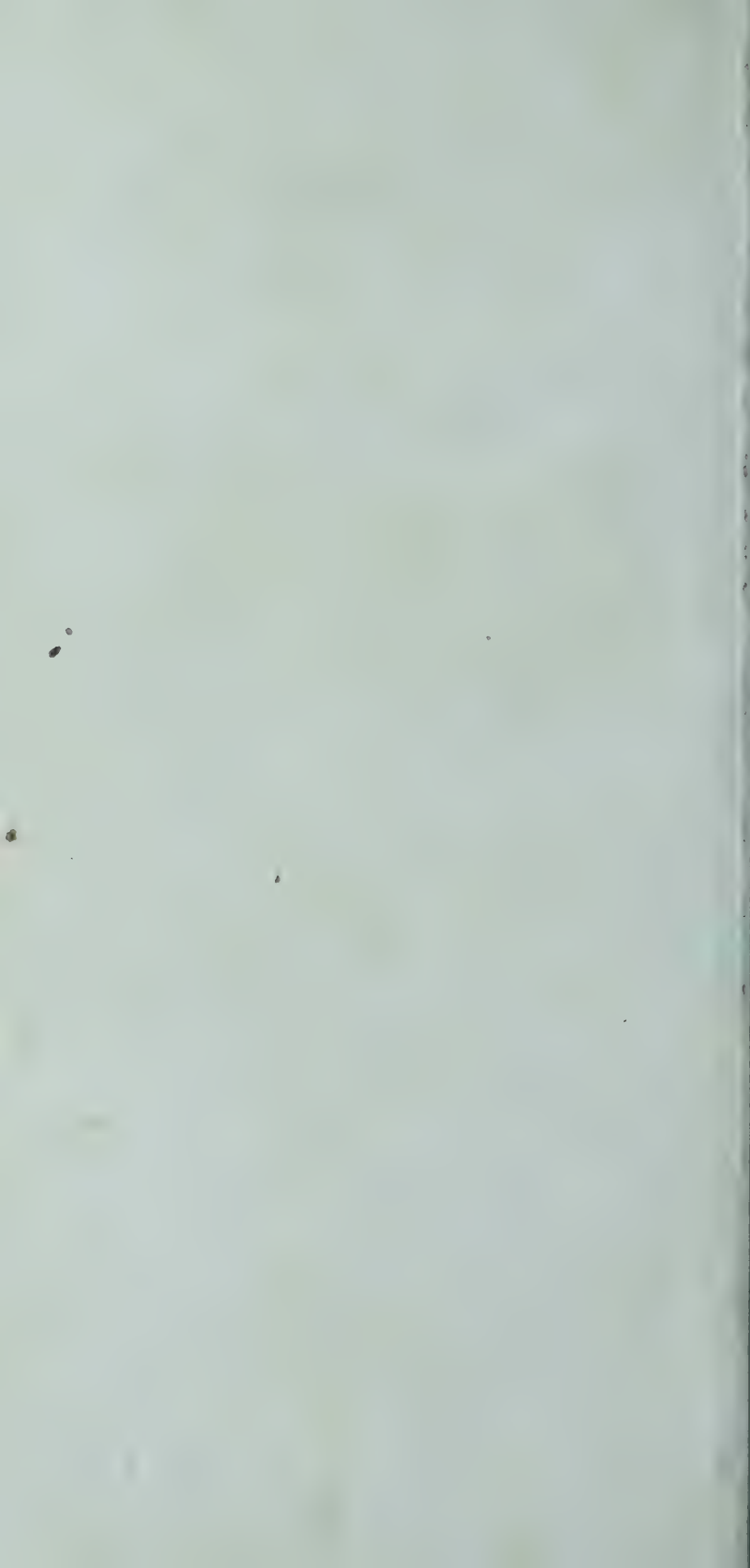
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